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HIGH-SPEED PHOTOGRAPHY OF VIBRATIONS (SOUND, MECHANICAL, ELECTRICAL, ETC.).*

BY

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Up to within a few years ago I shared what I believe to be the general feeling among technical scientific men that photographic methods of recording experimental data such as pressure-volume changes in engine cylinders, motion or timing of valves, vibrations of sonorous bodies, motions of optical images or the interference fringes obtained with visible or ultra-violet light, etc., etc., could not be rendered sufficiently simple to be reliable in the hands of the ordinary intelligent mechanic. Nearly two years' experience in France during the war convinced me that photographic recording is the quickest, cheapest, most simple and cleanest method there is. In the American Army I was in charge of the sound-ranging service, the object of which was to locate the positions of the enemy large calibre guns by recording the time of arrival of their sound at known positions near our own trenches. An accuracy of about fifty feet in five miles was required and a delay of more than four or five minutes in recording, calculating and reporting to our own artillery headquarters was considered excessive. The work was carried on by the ordinary enlisted man who had been given but a few weeks' special

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training; and it was always conducted under rather unfavorable conditions in cellars of ruined houses or in crowded dugouts. I believe that photographic methods which stood this test continually for months without a breakdown are suitable for use under almost any conditions.

Success was chiefly due to the fact that all operations were made strictly automatic. The camera was designed to use a cheap sensitized paper which was fed from a 200-foot roll past a stationary lens through which the exposure was made. The paper was automatically developed and fixed before it left the camera, so that there was no chance whatever of confusion of records when a great many were being taken in rapid succession, since the operator could inspect and mark with a pencil each record as it issued from the camera. In the case of the camera originally designed for field use, the speed of taking the photograph was slow, so that the paper could be run through the developer and fixer at the same speed at which exposure was made, without danger that the development might not be long enough for the most satisfactory contrast between light and shadow. For laboratory purposes, however, it is desirable that very rapid exposures may be taken in some instances and therefore the camera was re-designed by Mr. William Duryea, head mechanician of the Physical Laboratory of Princeton University, whose great experience in the design and construction of the field instrument enabled him to retain the excellent simple automatic features which had been thoroughly tested, and, at the same time, introduce modifications which permit much greater flexibility in use. One of these is a simple mechanism which allows the record to be taken at one speed and developed at a slower speed so as to give sharp contrast. Exposure speeds up to about four feet per second, using an ordinary automobile electric-light bulb as a source of light, can be used and the automatically developed records show entirely satisfactory contrast.

A series of fine lines reaching clear across the paper is photographed at the same time as the record. These lines are spaced 0.01 second apart, even if the speed of the paper should vary slightly, and serve as time-lines to time accurately an event shown on the record; for example, the opening and closing of an exhaust-valve of a running automobile engine.

An automatic recording camera can be used to trace the motion of any moving part of a mechanism and, owing to the high speed at which a record can be taken, it is possible to study variations which occur in time-intervals as short as 0.001 second. It is more convenient to transmit electrically to the camera the motion that actually takes place in the mechanism than to attempt to set up the camera itself close to the mechanism. A special form of simple string galvanometer is very convenient and meets satisfactorily the necessary condition that its moving part shall move synchronously with the motion of the mechanism. The moving part of the galvanometer is practically weightless, as it is a short piece of wire 0.0004 inch in diameter, and its motion is strongly damped by the magnetic field in which it is placed. When a current is sent through this wire it moves in the magnetic field and a shadow of this motion is photographed by the automatic camera.

In practice, almost any slight motion can be converted into a flow of electricity, so that the applications of photographic recording to the study of vibrations in running machinery are very numerous.

CAMERA.

The essential features in the design of a suitable photographic recorder for the experimental purposes of a laboratory are somewhat similar to those embodied in the moving picture machine, in that a sensitized tape must be moved rapidly behind a suitable lens which brings an image of the moving object on the sensitized tape. In the moving picture camera an extended image of a variety of objects must be formed and a series of such extended images is obtained by the use of a shutter which revolves at suitable speed. The problem is somewhat simpler in the design of photographic recorder since the moving object which is to be photographed is, in general, very small compared to the moving objects photographed by the moving picture camera. It is, in fact, generally possible to arrange that the moving object shall be a point of light, or, at least, a fine line of light, whose long dimensions may be brought parallel to the direction of motion of the sensitized tape in the camera. Instead of a line or point of light, a sharply defined moving shadow caused by the motion of a very fine wire may be the object to be photographed. Under

these conditions there is not the possibility of overlapping of portions of the images on the sensitized tape that there would be in the moving picture camera and hence the usual shutter of such cameras may be dispensed with and an actual continuous record of the motion of the small body may be made instead of a series of instantaneous photographs of its position as would be the case were a shutter used. The possibility of doing away with the shutter greatly simplifies the design and permits the attainment of very rapid exposure without any serious mechanical difficulty.

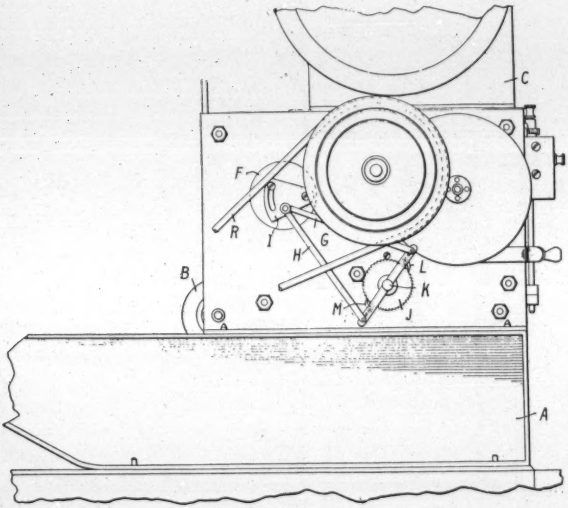
If it is desired to record the motion of a spot of light which moves, say, in a horizontal plane, an ordinary lens may be used to bring an image of the spot on the moving sensitized tape and the tape is run rapidly behind the lens in a vertical plane. This gives a photographic trace of the position of the spot in the form of a line. If a bright flash or a dense shadow is thrown across the tape every hundredth of a second, for example, it will be possible to tell from the developed record just what the position of the spot of light was at any given instant of time. If, instead of a spot of light, the moving object is a fine line of light or a sharply defined shadow in a vertical plane, it is necessary to substitute for the ordinary lens, to bring the image on the tape, a cylindrical lens whose axis (the axis of the cylinder from which the lens is cut) lies in a horizontal plane. The action of such a lens is to gather all of the light from a vertical line and focus it into a very bright and tiny spot and the lens has no condensing action in the direction of its own axis; therefore, the line of light is imaged as a spot of light whose diameter is the correct image of the diameter of the line of light. If there is no motion of the line the photographic record is a straight line which is the correct image of the stationary line. If the line moves rapidly the record shows a curve any point on which is the image of the position of the moving line at the corresponding time. If a sharp shadow is cast by an opaque narrow wire which moves, the motion of that shadow gives a curve on the record which is a faithful representation of the motion of the wire which casts the shadow.

Figs. 1, 2, and 3 show some of the especial features of a recording camera.

In Fig. 1, A is a trough with two compartments which serves as a base to the camera. In the compartment which extends from the extreme right of the figure to a point below B

the developer is placed. B is a roller which transfers the developed film into the second portion of the tank to the left of the figure in which the fixing bath is. The developed side of the film is the under side as it comes through the baths, and, for this reason, is sufficiently protected from daylight so that the fixing may be done outside the camera proper. The unexposed film is stored in the upper cylindrical portion of the camera (shown in

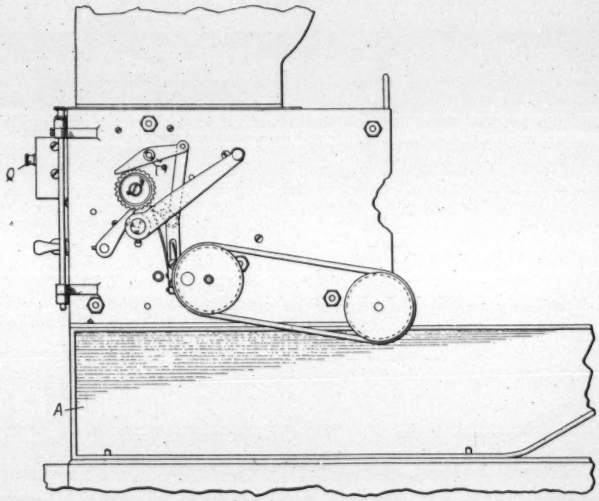
FIG. 1.



part near C) and is fed down in a vertical plane at the right of Fig. 1, being caught by the rollers D shown in Fig. 4 (in plan). If the speed of exposure is rapid, the rollers D are driven more rapidly than the rollers E by the mechanism shown at F to M inclusive in Fig. 1, which allows of any practical ratio of speeds. When the sensitized tape is started it immediately commences to be fed into the developer at the slower speed and the excess of tape is stored up in a storage space near the top of the camera. The tape passes between the blades of a knife operated by the lever N of Fig. 3, which cuts off the tape when the operator

has finished an exposure. When this happens the rollers D, Fig. 4, cease to feed the unexposed tape, but the rollers E and O continue to feed the exposed tape through the solutions until all has passed through. The mechanism, shown enlarged in Fig. 3, serves to guide the tape into the storage space and prevent its entanglement with a new length of tape in case it is desired to expose a second tape before the first one has passed through the camera. The face of the camera is closed by a hinged

FIG. 2.

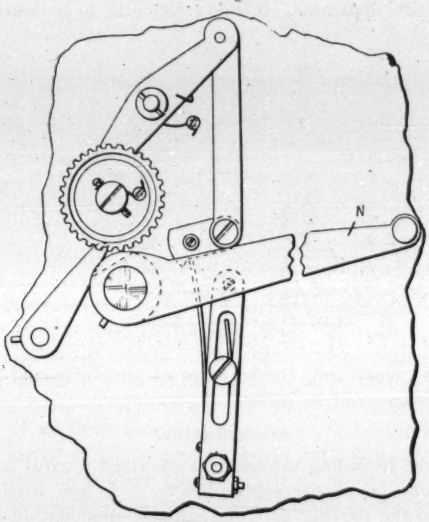


door—P, Fig. 4—which carries the cylindrical lens with its axis in a horizontal plane. The amount of light admitted to the lens is regulated by a horizontal aperture of variable width which can be opened or closed by a knurled screw Q, Figs. 2 and 4. The power necessary to drive the mechanism is supplied by a motor (not shown) which may be started or stopped by a foot switch controlled by the operator. This motor drives the mechanism by means of a belt R. Suitable gears, shown in Fig. 4, are used to drive the roller D at any desired speed.

TIME SCALE.

It is perfectly possible to feed the sensitized tape through the camera at practically constant speed, so that linear distances along the tape are approximately proportional to the time. However, it is easily possible to photograph on the tape itself an exceedingly accurate time scale in the form of lines across the record at right angles to the direction of motion of the tape. This may be done by causing a spoked wheel to revolve rapidly in

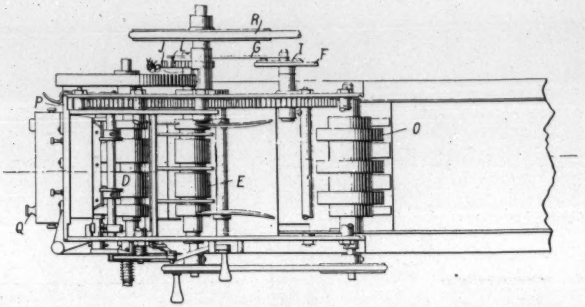
FIG. 3.



the path of the light with which the record is photographed. The rotation of this wheel may be governed by the motion of the prongs of an electrically driven tuning fork in such a way that a spoke of the wheel is brought parallel to the axis of the cylindrical lens at intervals of exactly one one-hundredth of a second. The shadow thrown by a spoke may be made to completely block off all light as the spoke comes into parallelism with the axis of the cylindrical lens and a sharp image of this shadow may be formed on the sensitized tape by means of an ordinary lens placed between the spoke and the cylindrical lens. By this means an

accurate time scale may be photographed on the tape at the same time as the record of the motion which is being photographed by the cylindrical lens is being made. In this way the accuracy of the time scale is in no way affected by unsteadiness of motion of the tape, since, were the motion to slow down due to friction, the spacing of the time lines would be less in distance but still the same in time interval. This devise is an old one known as the phonic wheel and has been used extensively in physiological and psychological apparatus though it has seemed to have found little use in physical apparatus. It leaves very little to be desired on the

FIG. 4.



score of accuracy and, on the score of simplicity and dependability, nothing could be better.

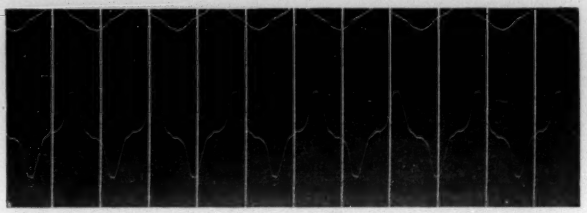
GALVANOMETER.

With the recording camera just described a great variety of motions may be photographed directly. A fine wire may be attached to the moving part and suitable illumination provided and a motion of the shadow of the wire photographed. Often it is more convenient to convert the motion which it is desired to record into a flow of electric current, to pass this current to a suitable galvanometer and to record the motion of the moving member of this galvanometer. If this is done, great care must be taken that the galvanometer used must not introduce motions characteristic of itself. The moving part of a suitable galvanometer must execute motions which are determined practically only by the current flowing and not at all by the inertion or elastic properties of the moving part of the galvanometer. That is, the

moving part must be practically without weight, it must have a restoring force acting on it which will make it return quickly to its position of rest, and its motion must be sufficiently damped so that it will not tend to overshoot its position of deflection as it takes up this position. In addition, it must be moderately sensitive so that small currents may produce appreciable motions.

It is impossible to fulfill all of these conditions absolutely, but they have been practically met in the design of the string galvanometer by the Dutch physiologist, Einthofen, and described by him in *Pflüger's Arch. f. d. Gesamte. Physiol.* (99, p. 472, 1903).

FIG. 5.



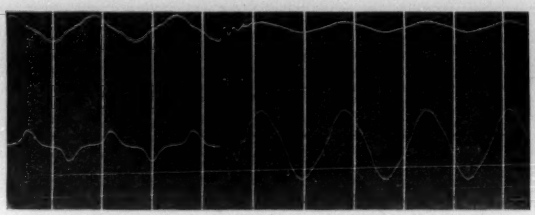
The full theory of the design and performance of the string galvanometer is also given in *Ann. der Phys.* (21, 1906, p. 483).

The instrument which I have used in connection with the recording camera is a simple modification of the Einthofen instrument. One or more very fine wires are mounted vertically between the poles of an electromagnet whose magnetic field is horizontal. The pole pieces of the magnet are bored out and each is fitted to carry a small microscope objective lens of about ½-inch focus, each lens being about ½ inch from the plane of the fine vertical wires. Light passing through the lenses travels at right angles to the plane of the vertical wires and along the lines of force of the magnetic field.

As a source of light a small nitrogen filled tungsten filament automobile head-light bulb is used. A small lens forms a real image of the filament at ½ inch from the first microscope objective mentioned above. Between the bulb and the small lens a spoked wheel is mounted so that the spokes, as they revolve, cut off the light. The spoked wheel is rotated at constant speed, so that a spoke comes into a horizontal position every hundredth of a second. The constancy of rotation of the wheel is secured by

governing its motion by current impulses from an accurate tuning fork, itself electrically driven. The light from the real image of the tungsten filament is rendered parallel by the first microscope objective and this narrow parallel beam of light illuminates uniformly the vertical fine wires of the galvanometer. These wires cast shadows which may be focussed by the second microscope objective so as to be sharp black lines in the plane of the photographic tape of the camera. A cylindrical lens is mounted in the converging beam of light so as to render the sharp shadow lines sharp shadow points as mentioned above.

FIG. 6.



When a current flows in one of the galvanometer wires, the wire moves at right angles both to its own length and to the direction of the magnetic field in which it stands, and since the beam of light is in the direction of the magnetic field, the motion of the wire is in a vertical plane and across the beam of light. The shadow of the wire will thus move across the axis of the beam of light or will move in the plane of the sensitized tape of the camera. For small currents the amount of motion of the point image of the shadow on the tape will be proportional to the current and a reversal of the direction of flow of current in the wire will produce a reversal of the motion of the shadow. It is possible to adjust the position of the wire in the magnetic field of the galvanometer so that the deflection of the shadow to the right and left of the zero position is accurately the same when a given current is sent, first in one direction and then in the other, through the galvanometer wire.

DAMPING.

If a small current be sent through the wire and a permanent deflection of the shadow image obtained, and then the circuit be

suddenly broken, the record of the motion of the wire as it returns to its zero position is a wave motion whose period is determined by the tension to which the wire is subjected and by the mass of the moving wire. The successive excursions of the wire about its zero position grow gradually less because of air friction, stiffness of the wire, etc. The motion of the wire on open circuit is only very slightly damped and the instrument would be wholly unreliable if used under these conditions, for the motions of the wire would be more characteristic of the tension and mass of the wire itself than they would be of the current flowing in the wire. The

FIG. 7.

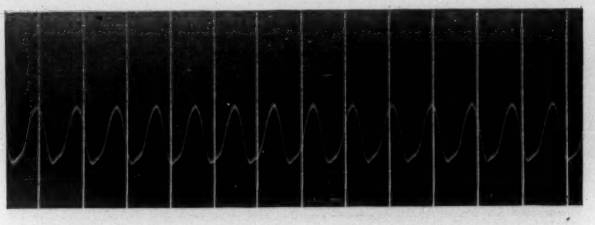
behavior of the wire will be quite different, however, if it is always shunted with a resistance comparable to its own resistance, for then, as the wire moves in the magnetic field it acts as a tiny dynamo and sends current through the shunting resistance, and the energy of this induced current must come from the motion of the wire. To the small air friction damping which exists when the wire is on open circuit, is added a large electromagnetic damping when the wire is shunted with a resistance comparable to its own resistance and the amount of this electromagnetic damping may be increased by reducing the resistance of the shunt. In practice it is possible to render the motion of the galvanometer wire practically aperiodic by the use of a shunt whose resistance is about one-third of that of the wire itself. This has the disadvantage of reducing the sensitivity of the galvanometer to about one-third of what it would be were no shunt used, but the gain in having a practically dead-beat instrument whose motion depends solely on the instantaneous value of the current flowing in it, more than offsets this sacrifice in sensitivity.

If one wishes to record very rapid variations in current, one must put the wire under rather strong tension so that its free

period (undamped) shall be less than the period of the current variations one wishes to record; at the same time one must shunt the wire with small resistance in order that the motion of the wire may be sufficiently damped so as to be practically aperiodic. Under these conditions the sensitivity of the instrument (deflection for a given current in the wire) will be relatively small, both because of the large tension and because of the low shunt.

If one has to record slow variations in current, one may relax the tension and secure adequate damping by the use of a higher

FIG. 8.



resistance shunt and the sensitivity under these conditions may be relatively very large.

It follows from these considerations that the electromagnet of the galvanometer should be designed to give as strong (and uniform) magnetic field as possible in the region where the wire (or wires) stands since both the sensitivity and the damping increase with increasing field strength. In the instrument constructed in this laboratory, great care has been given to this element in design and the results are very satisfactory since it is possible to obtain a sensitivity of about one one-hundred thousandth of an ampere per millimetre deflection of the shadow of the wire and still preserve sufficient quickness of response and damping to faithfully record small current variations as rapid as a few hundred per second.

So great a sensitivity as this is not needed for most laboratory purposes. When it is not needed a faithful record of current variations taking place in less than a thousandth of a second may be easily secured by increasing the tension and damping of the wire.

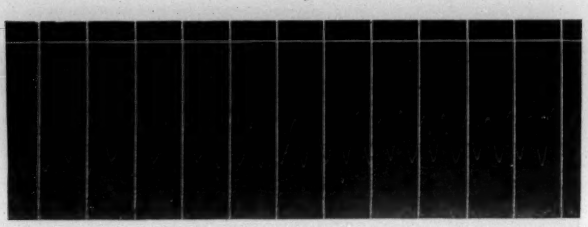
Examples of Use of Recorder.—

(*a*) As an oscillograph for current and voltage measurement with alternating currents.

If two wires are used, one may serve to record variations in electromotive force and the other to record current variations.

Fig. 5 shows a record of the voltage over the primary of small, cheap transformers with an iron core, and the current in the primary when the secondary is on open circuit. (In the following figures the voltage record is at the top and the current record near the middle of the tape and the beginning of the record is at the left-hand edge, so that each line on the time scale as one counts

FIG. 9.



towards the right, is one one-hundredth of a second later than the line to its immediate left.)

In this figure it will be noted that the current attains its maximum later than the voltage attains its maximum (*i.e.*, the current lags on the e.m.f. in the inductive circuit) and on measurement it will be seen that the lag is very nearly one-quarter of a period. It will be further noted that the current does not follow a simple sine law but shows evidences of hysteresis losses in the iron core of the transformer. Fig. 6 shows the effect of suddenly short-circuiting the secondary of the little transformer by placing a knife blade across its terminals (contact not very abrupt!). The effect is to reduce the impedance of the primary which is shown as an increase in the current and a decrease in the voltage, and to bring the phase of the current into practical agreement with that of the e.m.f. (*i.e.*, to reduce the angle of lag to zero), and also to make the current nearly a sine wave. Fig. 7 is the record of voltage over, and current through, a small telephone condenser of about two microfarads capacity, and the current will be seen to lead on the e.m.f. by about a quarter of a period; also the distorsions of the current wave from the sine form owing to har-

monic components for which the reactance of the capacity is less than for the fundamental are easily noticed.

(*b*) Records of Musical Notes.

In Figs. 8, 9 and 10 are shown records of the flow of current in an ordinary telephone microphone when an open organ pipe was blown near the microphone. They are thus approximately similar to the wave form of the notes given out by the organ pipe.

Fig. 8 shows the fundamental note of a large pipe giving 113 vibrations per second.

Fig. 9 is another record of the same pipe giving the octave 226 vibrations per second.

FIG. 10.

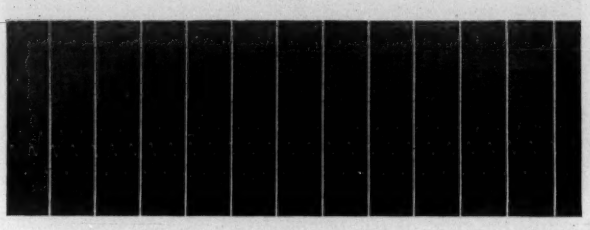


Fig. 10 shows the octave and double octave of the fundamental note of the pipe.

Fig. 11 is a record taken when the pipe was very strongly blown and giving a variety of overtones, the most rapid of which is 904 vibrations per second.

The great regularity with which vibrations repeat themselves is not to be wondered at in the cases shown in records 5, 6 and 7, for the alternating current was furnished by a large engine in a central power station, but the regularity exhibited in records 8, 9 and 10 is rather surprising in view of the fact that the primary curve was a blast of air in an organ pipe. Not only the frequency remained constant, but also the quality of the note remained the same in succeeding vibrations.

(*c*) Records of pressure and volume changes in cylinder of high-speed internal combustion engines.

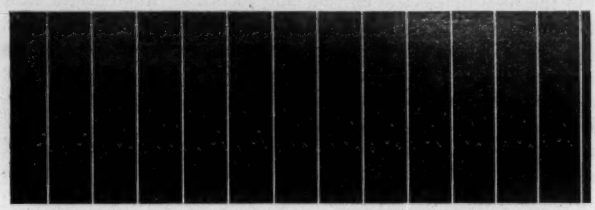
The recorder has been used with considerable success in the study of the causes of the " fuel knock " in automobile engines.

To discuss details would lead beyond the scope of this paper, but one or two points about the design and construction of suit-

able indicators for measuring rapid changes in pressure will not be out of place.

What has been said above about the necessity of securing aperiodicity in the wire of the galvanometer described in this paper holds with equal force in the case of the design of a suitable indicator to record rapid fluxations of pressure: The indicator must indicate the pressure to which its moving part is subjected, and it must not have any mechanical peculiarities of its own which might be mistaken for true pressure variations. In other words, it must be sufficiently damped so that its motions are aperiodic, and it must be stiff so as to have a quick period of return to its

FIG. 11.



position of rest. One way in which these properties may be obtained is to have a small capsule fitted so as to screw into a pet cock opening of a cylinder and to close the other end of the capsule with a stiff disk of steel. A second capsule above the steel disk may be designed so as to insure that the disk as it moves shall move a quantity of air or other fluid through narrow passages in order to provide some damping action to the motion of the disk. The entire double capsule is water-jacketed so as to prevent heating due to the hot gases on the side of the disk next to the engine cylinder. The disk may be shaped so that its bending (if small) is proportional to the pressure exerted by the hot gases in the cylinders.

Indicators built on this principle have been in use for some time. Most of these have measured the bending of the disk either by the use of a train of delicate levers or by a combination of levers to move a mirror from which a beam of light is reflected to a photographic plate. These methods are not free from theoretical and practical difficulties since it is difficult to insure that the levers themselves do not introduce lost motion and so produce vibrations

in the record which are not due to pressure changes in the cylinder, and moreover, any recording mechanical indicator attached directly to a running engine shares the not inconsiderable vibration of the engine itself and, unless it is very massive and rigid, is likely to give a record on which the mechanical vibrations are impressed on the pressure changes it is designed to record. Massive construction of the recording indicator is an undesirable feature for the reason that quick changes from one cylinder to another of a running engine are rendered difficult.

It seemed to me, therefore, desirable to retain the disk form of indicator and eliminate the objectionable lever feature and, naturally, I thought of converting the motion of the moving disk into the flow of electric current and recording this current flow with the recording galvanometer described above. This would allow the indicator proper to be small and easily screwed into a pet cock opening and it would allow the recording part of the apparatus to be set up at a distance from the noisy running engine. To secure this, all that was necessary was to fasten a very small coil of fine wire to the disk and into the coil to place one pole of an electromagnet, the other pole of which was a ring which surrounded the outer circumference of the coil of fine wire. In this way, when the disk moved, it moved all the turns of the fine wire coil across a radial field of magnetic force and an electromotive force was generated proportional to the velocity with which the disk moved. If the coil of fine wire was connected so as to send current through the wire of the galvanometer, this current, and hence the motion of the galvanometer wire, was proportional to the *velocity* of motion of the indicator disk, but the *velocity* of this disk is proportional to the *rate of change of pressure* occurring in the cylinder, so the final result was that the photographic record obtained gave the time rate of change of the pressure in a cylinder at every instant of time. A conveniently placed make-and-break key, placed on the crank shaft of the engine, could be used to send a small current to a second wire in the galvanometer and thus the times at which the cylinder was at any part of its stroke (say in-centre) could be recorded at the same time that the pressure variations were recorded. From these data the pressure corresponding to any given volume of gas in the cylinder can be calculated. However, in a study of changes brought about by changed mixture-strength, changed engine

speed, changed temperature or the like, it is not necessary to convert the observed data into the well-known pressure-volume diagram, for one soon becomes expert in interpreting the observed diagram which gives time rate of variation of pressure as a function of time. In fact, such an indicator diagram shows far more of what is going on in an engine cylinder than the corresponding pressure-volume diagram with which engineers are more familiar. One reason for this is that the most interesting part of the cycle of an internal combustion engine is near the in-centre and out-centre positions, for near the former the ignition takes place and near the latter the exhaust valve opens. The standard pressure-volume diagram is most crowded together at these very points, whereas a pressure-change-time diagram is perfectly uniformly spaced. The pressure-volume diagram is widely spaced in the very region where one could stand crowding without sacrificing accuracy and is so crowded together as to be inaccurate at the very places where the most important changes are going on in the cylinder. The pressure-volume diagram was designed for use with slow-speed steam engines and has certain obvious advantages, but it should be discarded when one wishes to represent what goes on in a high-speed internal combustion engine.

In the interests of fuel economy, it is very desirable that far-reaching studies be made looking towards increasing the efficiency of the automobile engine. Automobile engineers should not overlook the fact that the design of efficient steam engines was greatly aided by the perfection of a suitable indicator and that, while the problem of design of an indicator suitable for the high speeds of the internal combustion engine is difficult, it is by no means impossible.

Short Electric Waves. E. F. NICHOLS and J. D. TEAR. (*Phys. Rev.*, July, 1922).—By using the famous Hertzian oscillator with the addition of certain new features it has become possible to produce at will waves of length 1.8 mm. The shortest obtained was .8 mm. in length, but this was not reproducible. It is interesting to note that in two cases Nichols, in collaboration with another physicist, has expanded and perfected the work of Peter Lebedew, *viz.*, in the measurement of the pressure of light and now in the production of short electric waves. G. F. S.

Breath Figures. T. J. BAKER. (*Phil. Mag.*, October, 1922).—"If one breathes upon a sheet of glass which has been cleaned with soap and water and polished with clean linen, water-vapour condenses uniformly on the glass in such manner that the surface as seen by reflected light appears dull and rather white. If the tip of a small blowpipe-flame is made to traverse the surface of such a plate and the plate is then breathed upon as soon as it is cold, a whitish deposit appears on those parts which the flame has not touched, whilst the track of the flame is marked by a form of condensation which, owing to its transparency, appears black by contrast with the neighboring parts." A generation ago this phenomenon was discovered but its cause is not yet known. The extent of our knowledge of this subject is greatly increased by the studies made public in this paper. It is found that not glass alone but also porcelain, rock-crystal, mica, Iceland spar, platinum, nickel, silver, brass and mercury can be used. Aitken suggested that a change in the character of the surface is responsible, but this cannot be true since platinum and rock-crystal act as glass does. Again, a blowpipe-flame might well leave a slight solid deposit on its path over the glass, but this deposit is not necessary for the formation of breath figures since a hydrogen flame is just as effective. On the other hand, the figures are not obtained at all, or at most, to an imperfect extent, when chemically cleaned glass is used. The treatment with soap and water and linen leaves something on the surface that is needed for the production of the effect, and the flame removes some or all of this.

The most striking discovery of the author is that the condition that makes one glass plate capable of showing breath figures can be transferred to another. A plate that had been traversed by a flame was put in contact with another that had not been so treated. "Next day the plates were separated, and it was observed that both plates gave breath figures, one being an exact copy of the other. Moreover, the original showed no diminution of intensity." Later it was found that only a few minutes were needed for the perfect transfer when the plates in contact were under low atmospheric pressure. Even with an interval of 2 mm. between the plates a transfer was obtained. In one case a plate produced a transfer eighteen days after it had been treated with a flame. "Since the process is hastened by reduction of pressure and by rise of temperature, and occurs even when the plates are not in contact, it is clear that some gaseous material passes from one to the other." In spite of his long familiarity with the effect and of his intimate acquaintance with all that is known concerning it, he is unable to present a theory of the phenomenon that is satisfactory to himself. He has varied the surface on which the figures form and the nature of the flame. Why not employ for the third stage of the process something not so complicated in its origin as the human breath? G. F. S.

A STUDY OF NITROCELLULOSE.*

BY

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INTRODUCTION.

THE experiments of Bingham and Durham [1] with suspensions of infusorial earth, clay, and graphite in water and in ethyl alcohol seemed to prove that the fluidity is a linear function of the concentration; and that independent of the temperature, there is a certain concentration at which the material exhibits zero fluidity. This concentration seemed sharply to demarcate viscous from plastic flow. This conclusion seemed to be confirmed on analysis of the data on asphalt in benzene by Richardson,[2] sulfur in water by Oden,[3] malt flour in water by Lüers and Schneider,[4] sodium palmitate in water by Farrow,[5] glycogen in water by Bottazzi and d'Errico.[6]

At one time there seemed to be no escape from this reasoning, but recent knowledge of plastic flow necessitates our viewing with suspicion all viscosities of colloidal solutions where the flow was measured at a single shearing stress; for it has been shown [7] that in many instances a change in the shearing stress will entirely change the magnitude of the apparent fluidity. In order to measure the fluidity of a liquid, it is therefore necessary to use two or more shearing stresses, provided that there is any question as to whether the liquid is a colloidal solution or not.

It has been abundantly proved by many experimenters that, in *true solutions*, it is necessary to measure the flow at one shearing stress only in order to obtain the correct fluidity. This fact, however, should not lead us to assume that the same simple relations hold in *colloidal* solutions. For it seems, *a priori*, inevi-

* Communicated by Dr. Bingham.

[1] *Am. Chem. J.*, **46**, 278 (1911).

[2] "Fluidity and Plasticity," p. 205.

[3] Do., p. 204.

[4] Do., p. 290.

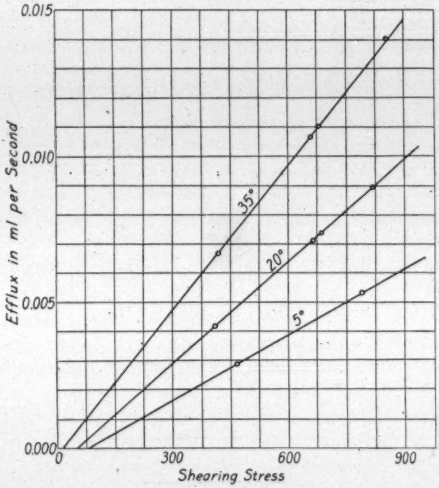
[5] Do., p. 291.

[6] Do., p. 207.

[7] Do., pp. 52, *et seq.*, 240, 279.

table that in a given instrument, the material which just seems to exhibit zero fluidity at a given shearing stress will again begin to flow when the shearing force is considerably increased, making possible the calculation of a new and different value for the fluidity. Hence there is reason for believing that fluidities of colloidal solutions as ordinarily measured are really a function of the shearing stress and therefore *apparent fluidities* only. They

FIG. 1.



The efflux-shearing stress curves at 5°, 20°, and 35° for a 7.708 per cent. dispersion of nitrocellulose in acetone.

stand in need of correction in order that they may become truly constants of the material studied. The whole subject is in need of investigation to prove first of all whether the fluidity is a function of the shearing stress, as seems probable.

MATERIALS AND APPARATUS USED.

It seemed best to work with both a suspension—(or non-polar) and an emulsion—(or polar) colloid. As a type of the latter for study in this paper, we have chosen nitrocellulose. It is easily obtainable in a sufficiently pure condition, its so-called "solutions" are quite stable from the physico-chemical point of view,

and the results of our investigation promised to have a practical bearing in various industries. The material was pyroxylin, containing 12.11 per cent. nitrogen, kindly supplied us by the E. I. du Pont de Nemours and Company. It was dried for eight hours in an oven at not over 50° C., and thereafter kept in a vacuum desiccator over sulfuric acid.

Acetone was used as the dispersion means, the sample being obtained from bisulfite compound in the Eastman Kodak Research Laboratory and by us merely dried over calcium chloride and distilled. The corrected and reduced boiling point was found to be 57.1° C.

The solutions were made in a 100 ml. flask closed by means of a tight-fitting stopper, and shaken for four hours on a shaking machine. Weighing after the operation was over proved that evaporation had not taken place. The solution was allowed to stand for twelve hours before use, and the clear solution was then carefully pipetted off for use.

THE MEASUREMENTS.

The measurements were made on viscometers Nos. 3, 6 and 7, the use of which has already been sufficiently described.[8] The shearing stress at the wall of the capillary is obtained from the following relation:

$$\pi R^2 P = 2\pi RlF$$

whence

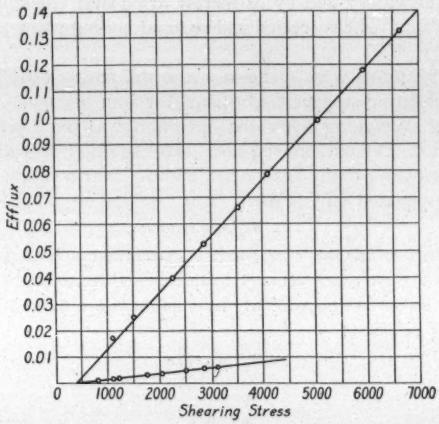
$$F = \frac{R}{2l} P.$$

With a concentration of only 1.39 per cent. by weight of nitrocellulose, the fluidity, at 30° C., was measured in the ordinary manner at three different pressures as measured on the manometer. With a pressure of 403.6 g. per cm.^{2} the fluidity was 52.49, at 214.6 g. per cm.^{2} the fluidity was 51.31, whereas at 62.96 g. per cm.^{2} the fluidity was only 50.76. The difference between the extremes is 1.73, which is 3.3 per cent. of the mean, but the experimental error amounts to only a few tenths of one per cent., so considering the steady increase in the fluidity with the pressure it is made probable that even a very dilute nitrocellulose solution behaves like a plastic material in that the fluidity is a function of the shearing stress.

[8] "Fluidity and Plasticity," p. 76.

The efflux expressed in ml. per second is found to be a linear function of the shearing stress (Fig. 1), as has already been found to be the case with many plastic materials. When the shearing stress is extrapolated to its value when the efflux is zero, we obtain the friction or yield value f. It may be defined as the shearing stress at the wall of the tube necessary to start the flow, assuming that the curve is linear throughout its entire length.

FIG. 2.



Efflux-shearing stress curves of anti-rust black paint with capillaries of different dimensions. The radius of No. 10 is 0.0147 cm. and that of No. 11, 0.036 cm. The length of No. 10, is 3.05 cm. and that of No. 11 3.04 cm.

The yield value has already been proved to be independent of the length or radius of the capillary through which the flow takes place. Thus Bruce measured the flow of an anti-rust black paint,[9] using capillary No. 10 with a length of 3.051 cm. and a radius of 0.01469 cm. and capillary No. 11 with a length of 3.041 cm. and a radius of 0.03062 cm. By the graphical method the same yield value of 360 dynes per cm.^{2} was found for both, and the mobilities were 0.796 for No. 10 and 0.795 for No. 11 capillary. (Cf. Fig. 2.) The mobility μ is calculated by means of the formula [10]

[9] *Proc. Am. Soc.*, "Testing Materials," 1922.
[10] "Fluidity and Plasticity," p. 225.

$$\mu = \frac{4V}{\pi R^2 (F-f) t}$$

where V is the volume of efflux in the time t, R is the radius of the capillary and F is the total shearing stress in dynes per cm.^{2}

DATA.

The results obtained are given in the following tables. Three viscometers were used, whose principal dimensions are as follows:

TABLE I.

	Radius of capillary in cm.	Length of capillary in cm.	Volume of efflux in ml.
Viscometer No. 3.....	0.01029	7.5	4.00
Viscometer No. 6.....	0.03202	13.75	4.00
Viscometer No. 7.....	0.03512	13.15	4.00

TABLE II.

The Fluidity of Pure Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Press. g. per cm.^{2}	Fluidity.	Spec. Vol.
10°	241.9	103.7	278.8	1.2435
20°	218.7	103.2	309.6	1.2616
30°	199.1	102.6	342.3	1.2804

TABLE III.

Plasticity of 1.073 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
20°	284.0	256.1.	1.5	64.63
20°	271.1	266.0	1.5	65.16
20°	311.1	233.4	1.5	64.75
20°	367.9	198.6	1.5	64.42
20°	454.4	161.8	1.5	64.13
20°	619.0	120.2	1.5	63.43
				64.59 Ave.

TABLE IV.

Plasticity of 1.39 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
30°	329.9	271.7	1.5	52.40
30°	634.7	144.5	1.5	51.47
30°	2189.2	42.46	1.5	52.04
30°	1003.2	91.23	1.5	50.44
				51.59 Ave.

TABLE V.

Plasticity of 2.743 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 7.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.²	Friction Dynes per cm.²	Mobility.
15°	79.5	147.0	1.5	.10.16
15°	185.3	63.99	1.5	10.15
15°	185.3	63.99	1.5	10.15
15°	249.5	47.17	1.5	10.08
				10.14 Ave.

Viscometer No. 6.

20°	286.3	48.59	1.0	11.39
20°	155.1	89.21	1.0	11.34
20°	201.0	68.82	1.0	11.41
20°	103.7	131.90	1.0	11.44
				11.39 Ave.

TABLE VI.

Plasticity of 3.98 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.²	Friction Dynes per cm.²	Mobility.
10°	151.2	316.2	6.0	3.31
10°	260.9	188.4	6	3.33
10°	725.8	69.5	6	3.36
				3.33 Ave.
20°	557.4	69.6	5	4.31
20°	248.7	154.1	5	4.18
20°	154.9	242.9	5	4.21
				4.23 Ave.
30°	120.1	243.3	4	5.39
30°	187.0	158.9	4	5.38
30°	476.0	63.5	4	5.47
				5.41 Ave.
40°	371.3	63.7	3	6.64
40°	371.3	63.7	3	6.62
40°	110.5	208.4	3	6.67
				6.64 Ave.

TABLE VII.

Plasticity of 4.966 Per Cent. Nitrocellulose by Weight in Acetone.
Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.²	Friction Dynes per cm.²	Mobility.
20°	314.1	259.8	8	1.96
20°	261.7	309.0	8	1.97
20°	510.0	162.9	8	1.93
20°	1342.6	63.1	8	2.09
				1.99 Ave.
35°	579.0	97.6	4	2.85
35°	319.1	174.6	4	2.86
35°	181.7	299.6	4	2.89
				2.87 Ave.

TABLE VIII.

Plasticity of 7.708 Per Cent. of Nitrocellulose by Weight in Acetone.
Viscometer No. 6.

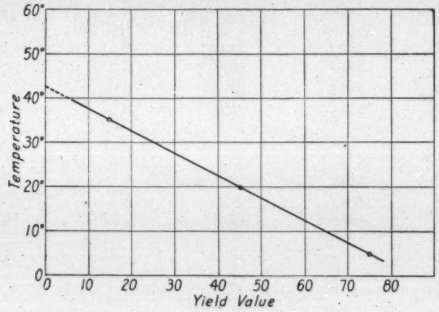
Temp. C.	Time seconds.	Shear. Stress Dynes per cm.²	Friction Dynes per cm.²	Mobility.
5°	1373.0	464.6	75	0.290
5°	744.6	797.3	75	0.288
				0.289 Ave.
20°	964.1	411.3	45	0.440
20°	540.4	684.9	45	0.448
20°	561.0	663.2	45	0.447
20°	422.8	839.6	45	0.465
20°	442.4	815.7	45	0.455
				0.451 Ave.
35°	593.4	413.3	15	0.656
35°	373.0	655.4	15	0.649
35°	357.0	679.4	15	0.654
				0.653 Ave.

DISCUSSION OF RESULTS.

Analysis of the data shows that the efflux is a linear function of the shearing stress, Fig. 1. As the concentration is increased or the temperature lowered the yield value invariably increases. In a few cases the mobility is not constant to within the normal experimental error, but there is no perceptible drift of the values

with the shearing stress. Shreds of undissolved cotton will of course give rise to erratic values.

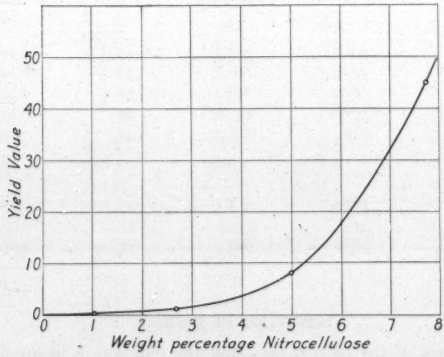
FIG. 3.



The variation of the yield value in dynes per cm.² with the temperature Centigrade, for a 7.708 per cent. dispersion of nitrocellulose in acetone.

On plotting the yield value against the temperature, Fig. 3, for our 7.708 per cent. mixture, there is indicated a sharp transition temperature at 43° C. where the yield value becomes zero,

FIG. 4.

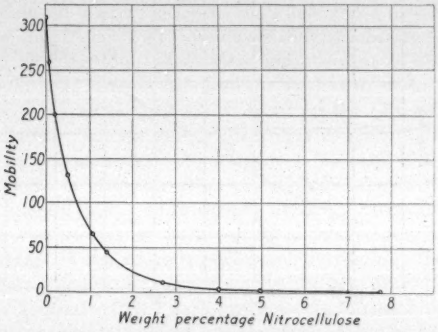


Variation of the yield value with the concentration of 20° C. of nitrocellulose dispersed in acetone.

i.e., where the material loses its plastic character and becomes a viscous liquid. The question suggests itself, "Does the colloidal solution become a true solution at the transition temperature?"

We hope later to investigate the effect upon this transition point of using other varieties of nitrocellulose and other solvents. The yield values for the lower concentrations are too inexact to give us certain information as to the effect of concentration of the nitrocellulose on the transition point; but since all of our solutions have a measurable though very small yield value even at 40°, there is nothing inconsistent with the view that the transition point is independent of the concentration. It is hoped that this transition temperature may serve as a useful criterion, and there is evidence that it may be used in colloidal solutions other than those of nitrocellulose.[11]

FIG. 5.



Variation of the mobility with the weight concentration at 20° C.

The yield value increases rapidly with the concentration, Fig. 4, but not in a linear manner. This is in marked contrast with the behavior of a clay suspension,[12] which is the only case we have to compare with this. A possible relation between the two will be brought out in the next paper.

The mobility of nitrocellulose dispersions is characterized by its extraordinary depression with very small percentages of the solid. Thus a one per cent. solution has a mobility which is only twenty per cent. of the fluidity of the pure solvent, and in an eight per cent. solution the fluidity is lowered to about one-tenth of one per cent. of it original value. This is one of the

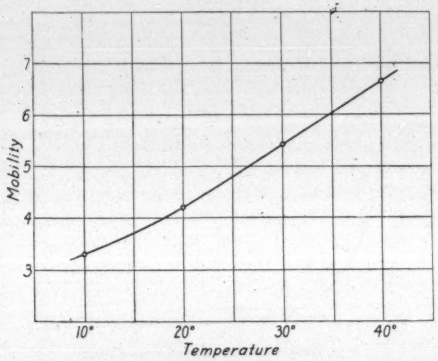
[11] "Fluidity and Plasticity," p. 289.

[12] Do., pp. 220 and 221.

most noteworthy distinctions between the polar and non-polar type of colloid. The relation between mobility and concentration is by no means linear (Fig. 5), the first additions of nitrocellulose being much more effective than the later ones.

The mobility increases with the temperature in a nearly, although not quite, linear manner (Fig. 6). From 10° to 40° the mobility of a 3.98 per cent. solution increases from 3.33 to 6.64, some 66.6 per cent. Over the same range of temperature acetone increases in fluidity from 279 to 373, or 28.8 per cent. The increase in mobility is therefore only partly due to the in-

FIG. 6.



The variation of the mobility with the temperature Centigrade of a 3.08 per cent. dispersion of nitrocellulose in acetone.

crease in the fluidity of the acetone, but it is due to an even greater extent to the solution of the nitrocellulose in the acetone.

In conclusion, we have found it possible to measure the plasticity of thin-flowing materials in the viscometer. We have found that certain substances of colloidal character, which have hitherto been supposed to have a definite fluidity, do not behave like true liquids as measured in the customary manner. By using a variety of shearing stresses, simple relationships are obtained.

More than 1500 technically trained persons, according to reports to the United States Department of Agriculture, are employed in studying farming problems in the State agricultural experiment stations. In 1921, 400 publications were issued containing results of their work.

A THEORY OF THE STRUCTURE AND POLYMORPHISM OF SILICA.*

BY

ROBERT B. SOSMAN, Ph.D.

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INTRODUCTION.

ONE can nearly always find a few specimens of quartz about a research laboratory, and there never was a museum, however small, that did not have some specimens of "rock crystal." Here, I suspect, is the reason why we now have such a variety of physical data on quartz; everyone who invented a new apparatus or method found quartz a convenient standard substance on which to try out his invention. Silica glass, also, because of its scientific and its industrial interest, has been the subject of many measurements. Not so many data are at hand on the other crystalline forms of silica, but, all told, a good deal is known about their relations to one another.

This body of data furnishes particularly attractive material for the "indoor sport" of theorizing about the structure of matter, since the process of building up a successful combination of hypotheses is the more complex and intriguing, the greater the variety of data to be explained. In the very properly limited space of a journal article I shall attempt only to sketch the outline of what I consider to be a consistent theory, or set of hypotheses, concerning the structure and polymorphism of silica, and to show how these hypotheses explain a few of the better known properties of silica. It need hardly be said that each hypothesis cannot, at the moment, claim any large likelihood of permanence, because new facts, especially facts concerning the arrangement of the atoms in space and the structure of individual atoms, are rapidly being obtained. Nevertheless, if we can find a set of hypotheses which satisfies the large body of existing facts about silica, it may prove to be the permanent basis for a dependable theory which will need to be modified only in minor points.

* Communicated by Dr. Arthur L. Day, Director of the Geophysical Laboratory and Associate Editor of this JOURNAL. First presented at the general meeting of the American Chemical Society of Birmingham, Alabama, April 5, 1922; also before the Philosophical Society of Washington, November 4, 1922.

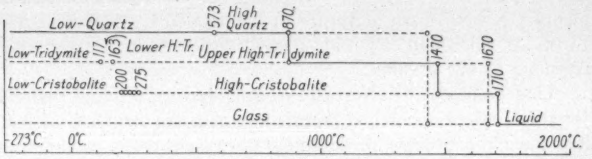
THE FORMS OF SILICA AND THEIR INTERRELATIONS.

At atmospheric temperatures and pressures there exist three distinct crystalline modifications of silica which have been recognized and studied in the laboratory,[1] namely, *quartz*, *tridymite*, and *cristobalite*. All three undergo enantiotropic inversions at higher temperatures; quartz has one such inversion; cristobalite, one; and tridymite, two, making a total of seven recognized crystalline modifications, to which must be added an eighth modification, the fused or glassy. The mutual relations of these eight are exhibited graphically in Fig. 1.

THE INDIVIDUALITY OF THE SiO_2 ATOM-TRIPLET.

Every chemist believes that there are certain groups of atoms, particularly groups containing carbon, which retain an individ-

FIG. 1.



Graphic representation of the relations between the forms of silica. (Solid lines represent stable states, dotted lines represent unstable states.)

uality in the gaseous, liquid, and crystalline states, whether the group be itself a pure substance, or a constituent part of a relatively complex compound. There is much evidence that this is true of the silica atom-triplet, SiO_2. I use "atom-triplet" instead of "molecule," since the word "molecule" has many connotations in which we are not now interested. This individuality of SiO_2 is recognized in our common groupings of chemical facts. In the text-books of chemistry the silicates are recognized as a proper subject for unified treatment, while the sulfates or chlorides are classified according to their metallic constituents. Under atmospheric conditions the silicates are nearly all transparent crystalline solids, insoluble in water and the usual solvents. They melt above a red heat to form viscous liquids of low volatility. Most of them are easily con-

[1] See especially Fenner, *Am. J. Sci.*, 36, 331–384, 1913.

verted into glasses, which are strikingly alike in many of their properties.

In an earlier paper [2] summarizing the temperature-composition diagrams of the commoner two- and three-component silicate systems, and commenting on some of their properties, I have emphasized the evidence furnished by those data in favor of the assumption that, in the silicates, SiO_2 acts as a unit. For the present the reader is requested to take that assumption for granted, as there is not space here to enter into a full discussion of this complex and much-argued question of the constitution of the silicates.

Assuming, as the basis of the argument, that the SiO_2 atom-triplet does retain its individuality in the silicates, we may reasonably expect that it will be found as an individual triplet in its pure crystalline forms, as well as in its liquid and vapor states. If this is true of the crystalline forms, it sets off silica as being markedly different from such strongly polar compounds as sodium chloride, for from X-ray studies it is now clear that a crystal of NaCl is a structure built up of Na and Cl atoms, or rather ions, and is a structure within which no definite groupings of atoms are recognizable. In crystalline silica and the silicates, on the contrary, definite triplets of the composition SiO_2 should be distinguishable.

The fact, however, that over a wide range of temperature silica in all its forms is an elastic solid, shows that some force prevents the free movement of each triplet as a whole and holds it in a fixed position in the crystal. The nature of this force is not entirely clear. In some crystalline compounds, no doubt, the process of forming the compound is one and the same with the process of forming the crystal, that is, the compound does not exist in the liquid or gaseous state. In others, the solid state may result entirely from the residual electric or magnetic field of permanent stable molecules. In silica, we shall assume that the solid state is the result of an interlocking or interpenetration of some of the electron orbits of neighboring atom-triplets.

Our ultimate problem, then, is to find the pattern according to which the silicon and oxygen atoms are arranged in space,

[2] R. B. Sosman, *J. Ind. Eng. Chem.*, **8**, 985–990, 1916; *Trans. Faraday Soc.*, **12**, 254–263, 1917.

and to find a manner of interlocking of electron orbits which will account (1) for the formation of the SiO_2 triplet, (2) for its building up into solid substances of several different forms, and (3) for the changes that it undergoes at the inversion points of the forms.

Our most direct information as to the arrangement of the atoms comes from X-ray diffraction, but we have relatively few data of this kind on silica. These will be discussed in the next section, after which the further development of the theory will be based on the polymorphism and physical properties of the forms.

EXISTING DATA ON THE POSITIONS OF THE ATOMS.

The analysis of crystal structure by means of X-rays has not yet been developed to the point where the structure of a complex substance of hexagonal, trigonal, or orthorhombic symmetry can be determined with the completeness and certainty which are possible for a cubic crystal. No atom-pattern, supported by X-ray refraction data, which would exclude the possibility of other atom-patterns, has yet been put forward for any of the modifications of silica. It is still necessary to fall back upon the procedure of theorizing about the shape and dimensions of SiO_2 and to adopt the result which best fits the known properties.

Bragg [3] has measured the angles of reflection of X-rays from the faces of a quartz crystal and has suggested that the data may be explained by means of a threefold hexagonal lattice, namely, three interpenetrating hexagonal lattices derived from each other by equal translations parallel to the axis *c*, together with rotations of 120° about that axis. There would be three SiO_2 atom-triplets to each unit of structure, and each hexagonal lattice would locate the positions of one-third of the triplets. Two independent structures of this kind are possible, the one "right-handed," the other "left-handed" in its direction of rotation. The distance of the silicon atoms from the axis of rotation, and the relative positions of the oxygen atoms with respect to the silicons, remain undefined.

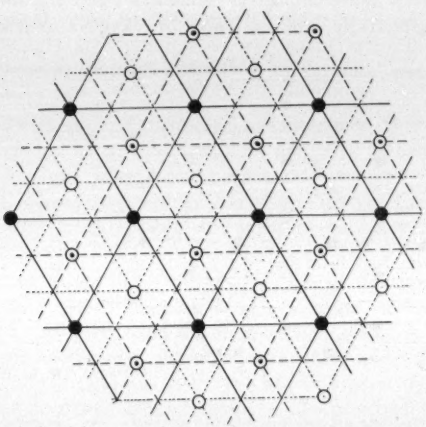
Bragg's structure does not satisfactorily explain all the optical properties of quartz, or its crystallographic growth-

[3] W. H. Bragg and W. L. Bragg, "X-rays and Crystal Structure" (London, 1915) p. 160.

forms. The structure suggested by Beckenkamp[4] better satisfies the optical and crystallographic requirements, and at the same time seems to be in agreement with Bragg's X-ray reflections.

Low-quartz,[5] according to Beckenkamp's structure, contains the *silicon* atoms in a rhombohedral lattice, which is in effect a threefold triangular prismatic lattice derived as shown in Fig. 2. Fig. 2 shows the plan of the structure, the trigonal axis being

FIG. 2.



Rhombohedral lattice of silicon atoms in low-quartz.

vertical. The solid circles represent one horizontal layer of silicon atoms; the centred circles, the next horizontal layer above the first; and the open circles, the third horizontal layer. The fourth layer is like the first, and so on. The rotation (which may be considered either right- or left-handed) is about an axis equidistant from the three kinds of circles. Thus far, the structure may be considered to be the same as Bragg's for the silicon

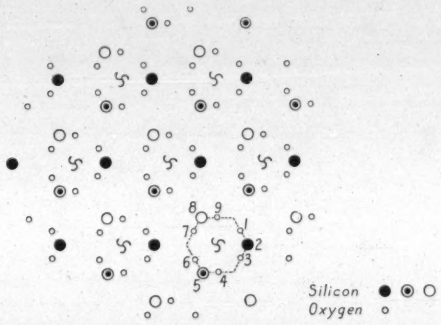
[4] J. Beckenkamp, *Z. anorg. Chem.*, **110**, 290–310, 1920.

[5] Divergent usage of α and β has created hopeless confusion in the nomenclature of silica. I have therefore dropped the Greek prefixes entirely, and use the English prefixes "high-" and "low-," as abbreviations, respectively, for "high-temperature-" and "low-temperature-."

atoms, with the distance of the silicons from the rotation-axis so defined that the right- and left-handed rotations are indistinguishable.

The positions of the oxygen atoms in the structure, however, depend upon whether the crystal is right-handed or left-handed. In right-handed low-quartz, the oxygens (and silicons) are situated as shown in the plan in Fig. 3. The lowest layer of atoms is numbered 1, the next above 2, and so on up to 9; number 10 being directly above number 1. Numbers 1 and 3, 4 and 6, and 7 and 9, respectively, are the pairs of oxygens associated with

FIG. 3.



Plan of the structure of right-handed low-quartz. The same silicon atoms are shown as in Fig. 2.

silicon atoms which are numbered 2, 5, and 8. The series of 9 atoms (3 SiO_2 triplets) thus forms a helix rotating upward to the right. The vertical planes in which the oxygen atoms lie are evident from the plan; viewed horizontally, the positions of the oxygens may be defined as lying upon the edges of the hexagonal prism containing silicon atoms of corresponding planes, that is, the first, fourth, seventh, etc., silicon planes.

On tridymite and cristobalite we have no X-ray data from which any conclusions as to the relative positions of the atoms can be drawn.

Before proceeding with the development of a theory which will link up the Bragg-Beckenkamp structure of low-quartz with

structures and mechanisms which will explain the relations of all the forms, it will be necessary to devote a few paragraphs to the general subject of polymorphism, with special reference to silica.

POLYMORPHISM.

The term "polymorphism" as currently defined and used applies only to the crystalline state. It is best defined as "that quality of a crystalline substance, having a definite chemical composition, which permits it to appear in modifications having different axial ratios or belonging to different classes of symmetry; changes which are relatively small and at the same time continuous, due to changes of temperature and pressure, are excluded.[6]

Hypotheses as to the cause of polymorphism have generally lumped together all its manifestations and tried to explain them by a single cause. The actual phenomena, however, show wide variations, which may well be traced to different causes. For example, two strongly contrasted types of polymorphism occur in silica.

There is, first, the "sluggish" type of inversion which occurs among the three modifications: Quartz, tridymite, and cristobalite. All three exist at atmospheric temperature and pressure, although only one, quartz, can be stable under those conditions. Nevertheless, the other two are very persistent and are not difficult to obtain experimentally. The principal feature of the inversions from one of these forms to another is their slowness, several hours usually being required for complete transformation, and at certain temperatures and in certain directions the presence of a solution or melt in contact with the silica is necessary before the change will occur at all.

[6] The Standard Dictionary (1913 revision, 1920 reprint) defines polymorphism as ".... the ability of certain substances to crystallize with different axial ratios without change of chemical composition." This would exclude an isometric substance which remained isometric through an inversion, for its axial ratio has invariably the value 1. It might also experimentally exclude a non-isometric substance, if one were to be found whose axial ratio did not change measurably through an inversion point. (This was at one time thought to be true of high-quartz and low-quartz.) Such modifications are, however, of different symmetry, so that the second criterion in the definition would apply.

The second type of inversion in silica is the "high-low" or "prompt-reversible" type, occurring between the high-temperature and low-temperature forms of quartz, tridymite, and cristobalite. These inversions occur promptly the moment the proper temperature is reached, although it should be noted that this temperature may be different according to whether the temperature is rising or falling; that is, they show a temperature-hysteresis. But, outside of this hysteresis range, the high-form is never found at a lower temperature, nor is the low-form found at a higher temperature. As pointed out by White,[7] the phenomena suggest some change which is common to all the three modifications, yet is affected by the transformation from one modification to another.

The hypotheses which have been advanced to account for polymorphism may be roughly grouped as (1) molecular, (2) structural, (3) atomic.

The molecular type of hypothesis assumes the existence of distinct molecules in the crystalline state, just as in the gaseous and liquid states. It has been most elaborately developed by Smits.[8] Having first shown experimentally that a dynamic chemical equilibrium between different kinds of molecules very probably exists in the liquid and crystalline states of certain substances, Smits' theory goes on to postulate such an equilibrium in every phase of every substance which exhibits polymorphism, and to apply thereto the well-known principles of the phase rule of Gibbs and Roozeboom.

The "structural" hypotheses assume that polymorphous forms of a substance differ simply in the arrangement of their constituent parts in the crystal lattice, whether those parts be molecules, atom-groups, or atoms (Bravais, 1851). Different orientation of the parts, without change of the arrangement in space of their geometrical centres, is also suggested as a variant of this type of hypothesis.[9]

The "atomic" type of hypothesis assumes that the polymorphous change is due to a change of form of some or all of the *atoms* of the substance, without necessarily any change in

[7] W. P. White, *Am. J. Sci.*, **47**, 31, 1919.
[8] A. Smits, *Die Theorie der Allotropie*, Leipzig, 1921.
[9] P. W. Bridgman, *Proc. Am. Acad.*, **52**, 91–187, 1916.

their arrangement or orientation. The change may be in the positions or orbits of the outside or planetary electrons, or it may be in the atomic nucleus itself.[10]

Now it need hardly be said that all these types of polymorphism may actually exist, one in one substance, one in another; or that there may be a real gradation from one type of polymorphism to another.[11] The inversion of benzil-ortho-carbonic acid at 65.7° might be taken as an example of polymorphism which is clearly molecular. The inversion of pure iron at 770° may be best explained as mainly an atomic inversion.[10] To anticipate the conclusions of subsequent sections of this article, the inversions of silica are best explained as partly structural and partly atomic, the sluggish type in silica depending upon a fundamental rearrangement of silicon and oxygen atoms, while the prompt-reversible type goes deeper into the atom but involves also a subordinate change in the relative positions of atoms.

In all this we must bear in mind what constitutes a real hypothesis. One of the most important objections to Smits' theory is the very facility with which it explains all the phenomena. There has been an uneasy feeling among some of those who have followed its development that the theory is capable of explaining not only all existing data on polymorphism, but any that can possibly be discovered. Now a theory which is capable of explaining all imaginable data in its field is, conversely, incapable of predicting any one experimental fact to the exclusion of any other; or, in the pragmatic philosophy, it is not a theory at all, but a form of words. It has happened more than once in the history of science that two formulas which sounded very different, but whose corollaries were experimentally indistinguishable, have led to needlessly long and bitter polemics. Hence it will be well to devote our closest scrutiny to what follows from a theory, rather than to the plausibility and general attractiveness of the formulation itself.

Among the dozens of clues which might give a hint as to the explanation of the polymorphism of silica, the following are particularly suggestive: (1) The coefficients of thermal expansion of the three high-forms are very small, in which they agree also with fused silica; (2) the high-low inversion temperatures are

[10] R. B. Sosman, *J. Wash. Acad. Sci.*, 7, 62-67, 1917.

[11] F. Rinne, *N. Jahrb. Min., etc.*, 1916, II, 96.

inversely proportional to the specific volumes of the three low-forms. Now a mechanically compact and stable atom-triplet, capable of taking up within itself most of the thermal vibration due to rising temperature, and so constructed that it can be used as a building unit in three different ways to make three space lattices of atoms, would account for the three high-temperature forms; then, if within each of these structures we can find an atomic binding mechanism common to all three, which mechanism is balanced against a force of thermal agitation tending to separate certain atoms in the structure, we can account for the high-low inversions and their dependence upon volume. At the same time, various properties of liquid, glassy, and colloidal silica suggest a thread or chain structure. The next step is to combine these various desiderata into a consistent whole.

STRUCTURE OF THE ATOM-TRIPLET.

All lines of evidence now indicate that an atom consists of a positive nucleus surrounded by electrons, whose number equals the ordinal number of the element in the Periodic System. The silicon atom consists of a nucleus with positive charge 14, surrounded by 14 non-nuclear electrons. The oxygen atom has a nucleus with positive charge 8, surrounded by 8 non-nuclear electrons.

The electrons are distributed as follows: In each atom there is an inner pair. The remaining 6 electrons of oxygen then form an outer group, while the remaining 12 of silicon form first a group of 8, and outside of that a group of 4. The tendency in both silicon and oxygen is toward the completion about each atom of a stable external octet, such as characterizes both neon and argon, the inert elements next in order of complexity above oxygen and silicon. This tendency causes the combination of silicon and oxygen to form SiO_2.

At this point theories of the structure of compounds begin to diverge. According to the Lewis-Langmuir theory,[12] the elec-

[12] In the development of the theory of silica I have used the Bohr revolving-electron type of atom. But since the Lewis-Langmuir fixed-electron atom (*J. Am. Chem. Soc.*, **41**, 868–934, 1919) is more familiar to chemists, the structure of SiO_2 will be expressed also in terms of that atom-type. That part of the theory of silica which is concerned with the structure of the triplet, and its building up into the solid modifications, would remain the same whichever type of atom be assumed.

trons occupy relatively fixed positions in the atom. The formation of octets, just referred to, is accomplished either by the transfer of electrons from one atom to another, or by the sharing of electrons between atoms.

My present hypothesis assumes that the silicon atom shares one pair of electrons with each oxygen, and the oxygens share a pair of electrons between them. At the same time the silicon shares one pair of electrons with each of two neighboring silicons.

FIG. 4.

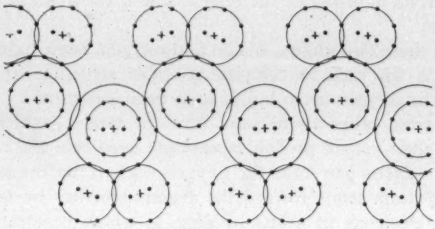
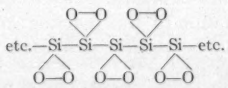


Diagram to illustrate the grouping and sharing of electrons in the silica thread (but not their positions in space).

The result is a *silica thread* built up of SiO_2 atom-triplets as the fundamental building unit. It may be crudely represented in a plane by means of the familiar valence bonds, thus:



or by some such representation as that of Fig. 4. This figure emphasizes mainly the grouping and sharing ideas, without attempting to represent the distribution of electrons in space. The orientation of the oxygen pairs is different in the different modifications of silica, as will appear below.

In terms of Bohr's revolving-electron quantum theory of atomic structure,[13] which now seems destined to replace the fixed-electron theories such as those of Lewis and Langmuir, the structure may be described as follows:

Around the silicon nucleus revolve two electrons in "uniquantous" (German *einquantige*) orbits. The stable structure of 10

[13] N. Bohr, *Zeitschr. Physik*, 9, 1–67, 1922.

electrons which characterizes the neon atom and constitutes the inner foundation of the silicon atom consists of this pair and two groups of 4 electrons in "biquantous" orbits, of which 4 are elliptical and 4 approximately circular (designated as orbits of types 2_1 and 2_2). These two groups of 4 biquantous orbits correspond numerically to the octet of Langmuir, but the octet is no longer considered as a "shell" of electrons. The remaining 4 electrons revolve in triquantous (type 3_1) orbits.

Similarly, in the oxygen atom there is an inner pair, a group of 4 electrons in orbits of the type 2_1 and 2 electrons in orbits of the type 2_2.

When these two atoms, silicon and oxygen, react together, the tendency is for each to complete a stable structure of electron orbits. The oxygen atom builds up a neon structure by taking 2 electrons from other atoms into orbits of type 2_2 which during a part of their course probably penetrate even into the region of the inner electron pair near the oxygen nucleus; in the same way the silicon atom tends toward the argon structure by taking on 4 foreign electrons in orbits of type 3_2 which penetrate to the neighborhood of the silicon nucleus.

The present hypothesis supposes that 2 of the electrons added to the silicon come from neighboring silicons, and the other 2 from the 2 oxygens; the 2 electrons added to each oxygen are drawn, one from the silicon and the other from the second oxygen. The formal representation of this bonding used with the Lewis-Langmuir theory may be equally well used, as a first approximation, with the Bohr theory.[14]

The resulting three atom-structures (one silicon and two oxygens) are roughly tetrahedral, because of the grouping of electrons of the "octet" in pairs, and the three are closely assem-

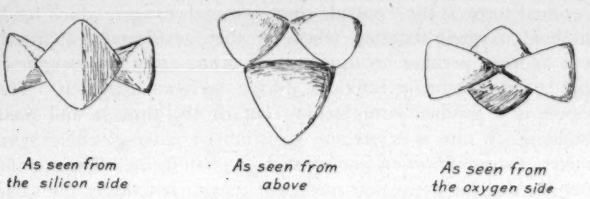
[14] See also footnote 12. Since this paper was presented, an article by Huggins on "The Crystal Structure of Quartz" has been published (*Phys. Rev.*, **19**, 363–368, 1922). This article presents no new experimental data, but proposes a very reasonable hypothesis of the structure, based on the Lewis-Langmuir hypotheses. It supposes that all the linkages between atoms in low-quartz are primary valence linkages between silicon and oxygen, making the crystal a continuous "molecule." The hypothesis offers no explanation, however, of any of the numerous other modifications of silica, or of the phenomena of the inversions; some of the arguments in its favor employed by its author in describing the structure of low-quartz would apply equally well to any of the other modifications, and all of them would apply equally well to high-quartz.

bled into an atom-triplet which is roughly trigonal. The sketch in Fig. 5 will give an idea of its form, if three interlocking solar systems can be said to have a form.

STRUCTURES OF THE VARIOUS MODIFICATIONS.

Liquid and Glassy Silica.—As already remarked, the present hypothesis supposes the silica atom-triplets to be joined up into threads. These threads form in the liquid state and their formation may begin even in the vapor. In the liquid they are in a constant state of vibration and movement, with the oxygen pairs in haphazard and probably varying orientation relative to the thread. A drop of silica glass in the neighborhood of 1700–

FIG. 5.



Sketch to aid in visualizing the shape of the SiO_2 atom-triplet.

1800° would resemble a mass of wriggling worms. The threads themselves not improbably have a helical twist.

If the temperature is rapidly lowered the threads become less and less active, until at last the mass becomes like a compressed pad of wires, and we have "solid" silica glass. An intricately tangled mass of wires has some of the properties of a solid, even though the individual wires are flexible.

The drawing out of a lump of such glass into a rod might naturally be expected to disturb the haphazard arrangement of the threads and give some of them a prevailing orientation parallel to the rod. This would explain the difference in expansion parallel and perpendicular to the axis in silica rods or tubes,[15] and the variation in expansion between different samples, indicated by some experiments. It perhaps will also aid in explaining the evidences of ribbon-like crystallinity in silica glass rods, observed

[15] Callendar, *Phil. Mag.*, **23**, 998–1000, 1912. The difference is usually not so great as the first measurements indicated.

by Rayleigh.[16] The thread hypothesis is also in accord with the familiar habit of amorphous silica of condensing in fine fluffy or lint-like forms. It has even been obtained from the electric furnace in microscopically fibrous massive form, a *fibrous glass*, which is wholly non-crystalline to an X-ray exposure of ordinary length,[17] though showing traces of a structure under longer exposures.

Cristobalite.—Suppose the cold silica glass reheated to a temperature in the vicinity of 1600°, which is below the melting temperature of cristobalite. The threads resume their active movements, but we must now take account of certain constraints upon these movements. The larger size of the silicon atom as compared with the oxygen distorts the latter so that there is a residual force at the "outside edge" of each oxygen which tends to hold oxygens together whenever they accidentally approach one another, perhaps because electron orbits from two neighboring oxygens actually interlock during such an approach. The result is a gradual straightening out of the threads and their building up into a crystalline structure of external cubic symmetry, the modification known as *high-cristobalite*. The specific volume and the expansion coefficient remain practically the same as for silica glass.

The silica threads are now assumed to lie parallel to a cube diagonal, that is, perpendicular to an octahedral face. Their relation to the cube will appear from the following considerations. Suppose the silicon atoms arranged in some variety of cubic lattice. Then imagine this structure turned up on one corner so that the octahedral normal is vertical. It may now be considered a rhombohedral lattice. For example, if the cubic lattice be a face-centred cube, its axial ratio considered as rhombohedral would be $a:c = 1:\sqrt{6}$ or $1:2.4495$. The vertical (trigonal) axis is assumed to be the axis of the silica thread, and the silicon atoms will be found to be arranged around it in helical fashion but in a helix which is considerably more drawn out lengthwise than in quartz. The oxygen pairs tend to orient themselves in the octahedral (now horizontal) planes, perpendicular to the axes of the threads. The direction of rotation of the helix,

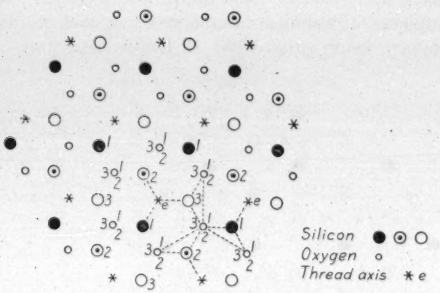
[16] *Proc. Roy. Soc.*, London, A **98**, 284–296, 1920.

[17] Photographs by Dr. E. W. Posnjak of this Laboratory.

whether right- or left-handed, is purely a matter of chance and the two kinds are probably present in equal amounts. The structure will be further discussed when we come to the high-low inversions.

Tridymite.—When the temperature falls below 1470° the diminished thermal agitation permits of a more stable configuration, namely, that of *high-tridymite*. The structure is hexagonal in external symmetry. The silica threads are parallel to the hexagonal axis, but are shrunken longitudinally, bringing the axial

FIG. 6.



Plan of the structure of high-tridymite. The same silicon atoms are shown as in Figs. 2 and 3.

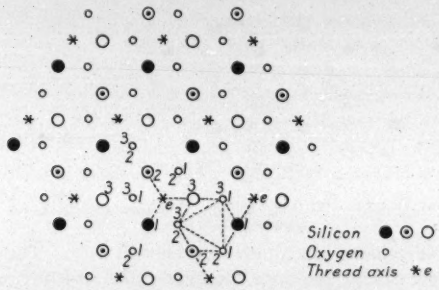
ratio for the silicon lattice down to about 1 : 1.7. The oxygens now assume definite positions throughout the structure, each pair lying in a plane perpendicular to the thread direction, and the lateral distance between the threads increases.

A plan of the structure is shown in Fig. 6. Successive planes of atoms are numbered 1, 2, and 3. It will be found that if the vertical axis *e*, along which the silicons are joined together, be taken as a centre of reference (which we might call an "electron-well" since the interlocking electron orbits between the silicons of a thread all cross this axis) the oxygen atoms occupy 6 "wells" all equally distant from the centre; all of these contain oxygens equally spaced along the vertical axis.[18]

[18] The structure is not in all respects satisfactory, since it may be necessary to assume twinning in order to account for the dihexagonal symmetry of high-tridymite. Beckenkamp also finds this necessary with his theoretical structure for tridymite, based on that of low-quartz. An untwinned structure would be better.

Quartz.—Further lowering of the temperature to 870° brings about still another rearrangement, producing the modification known as *high-quartz*. The structure is trigonal in external symmetry. The silica thread persists as in cristobalite and tridymite, but the silicon atoms have again been brought somewhat nearer together along the hexagonal axis. The essential change is in the position of the oxygens. These no longer occupy 6 wells around each electron-well, but instead occupy 3 close to the electron-well and another 3 farther away, and are arranged in vertical pairs, as is evident from the plan in Fig. 7, in which the successive planes of atoms are numbered 1, 2, and 3. The structure is rotatory, being either right- or left-handed.

FIG. 7.



Plan of the structure of high-quartz. The same silicon atoms are shown as in Figs. 2, 3, and 6.

General Remarks.—The foregoing structures for high-cristobalite, high-tridymite, and high-quartz agree well with the known interrelations of the forms, and the high-quartz structure fits on to that of low-quartz, as will be shown presently. For example, silica glass always crystallizes first to cristobalite, even in the tridymite and quartz ranges. Quartz likewise inverts directly to cristobalite even in the tridymite range, sometimes apparently passing through a stage of fusion. This is because the shaking down of quartz threads into amorphous threads by thermal agitation at high temperatures makes the formation of the relativity incomplete cristobalite structure (see page 760 following) a more easily attainable result than the rearrangement of the whole oxygen lattice to form tridymite; the tridymite recon-

struction requires time or the aid of a solvent. Again, right-handed high-quartz remains right-handed on cooling; although it sometimes becomes twinned, the twinning is always of the Dauphiné type, in which all the individual parts are right-handed or all left-handed, and never of the Brazil type, which is alternately right and left.[19] The cause of this is obviously the connection together of the two oxygens of the triplet; to make a right-handed crystal into a left it is necessary to disconnect the oxygens and move them around to the other side, which practically means disintegrating the quartz by means of a solvent, while the other type of twinning can be accomplished by merely rotating a part of the threads as units.

THE HIGH-LOW INVERSIONS.

As we have just seen, the maintenance of the crystalline structure of the forms of silica depends upon two constraints: First, the connection of the silicon atoms into threads; second, the attraction between the outer ends of oxygen atoms belonging to different atom-triplets or different threads. These constraints are similar in character in all three modifications.

The mechanism of the high-low inversion is likewise similar in all three modifications. The phenomena in quartz are the best known and furnish the most valuable clue to the atomic mechanism. Most, if not all, of the properties of quartz begin to change noticeably at a temperature considerably below the inversion, and progress according to a logarithmic law up to 573° where there is a sudden jump to an entirely different curve of change. As I have pointed out elsewhere,[20] this form of curve is duplicated exactly by the curve showing the relation between the angular velocity and the moment of the forces on two coaxial cylinders rotating in water. There is a limiting value of speed below which the moment is proportional to the speed, and above which the square of the speed enters, with a discontinuity separating the two states of motion.

An equally instructive analogy is found in the state of oscillation of two coupled oscillatory electric circuits, one of which is supplied by an electron tube.[21] In this case the curve of

[19] Beckenkamp, *op. cit.*

[20] *Amer. J. Sci.*, **37**, 19, 1914; *N. Jahrb. Min., etc.*, Beil. Bd. **40**, 139, 1915.

[21] Van der Pol, On oscillation hysteresis in a triode generator with two degrees of freedom, *Phil. Mag.*, **43**, 700–719, 1922.

current against the natural frequency of the secondary circuit, when the frequency is varied continuously, not only jumps suddenly at a certain point, but jumps back at a *different* point when the conditions of change are reversed. In showing this "oscillation hysteresis" the system duplicates exactly the behavior not only of quartz, but of all the high-low inversions of silica, since all show a definite "temperature hysteresis" in the inversion phenomena according as the temperature is rising or falling. This behavior is also duplicated by high-low inversions in iron and other substances.

Evidently some subsidiary part of the structure (triplet, atom, nucleus, or electron) is in a state of motion which varies with the temperature, but which influences the motion of some other subsidiary part in such a way that the secondary motion changes suddenly from one state to another. This performance probably does not take place mainly or entirely within the triplet, else all the forms of silica would have an inversion at about the same temperature. On the contrary, the inversion temperature is roughly inversely proportional to the volume of the low-form.

I have therefore assumed that the high-low inversion affects chiefly the "outside" linkage between oxygens which, under the present theory, is one of the two constraints holding the crystal together. We may then suppose the inversion (with rising temperature) to consist (1) in an increase of amplitude of the thermal vibration of a pair of oxygen atoms, which (2) influences the manner of revolution of a pair of electrons, with the result that (3) a relatively constant attraction between the two oxygens becomes balanced by an increasing repulsion between the two orbits in question. At a certain temperature the existing structure becomes unstable and the oxygens move suddenly to a new position characteristic of the high-form. Until we know more about the form and distribution of the 32 electron orbits which we assume to exist in each triplet, it will not be possible to specify more exactly the character of the change in the orbital motions. Perhaps it consists in the production of rotational vibrations of the plane orbits of the inner pair, which vibrations become actual rotations of those planes at the inversion point. This would be a possible electron mechanism to explain Ashworth's theory of

the high-low inversion in iron.[22] Experiments on the effect of an A. C. field upon the magnetic properties of quartz through the inversion point might throw light on this question.

Quartz.—In the structure of low-quartz (see p. 746) the plane of the silicon and the two oxygen atoms of a triplet stands at an angle to the hexagonal axis, bringing the oxygens of successive triplets near each other in what we might call "external pairs," to distinguish them from the "internal pairs" of the SiO_2 triplets themselves. Three such external pairs complete the circuit of the helix. As the temperature rises the increasing amplitude of vibration of the oxygen atoms finally brings about, at 573° C., a sudden change in the mode of revolution of certain electrons associated with the two atoms. The atoms are pushed apart into a new position in which they form vertical pairs, all equally distant from the "backbone" or "electron-well" of the thread of SiO_2 triplets. This simple change of shape of the SiO_2 triplet, which is all that the movement amounts to externally if the electrons are not considered, gives us the high-quartz structure already described.

Tridymite.—In the tridymite structure the oxygens are farther apart than in quartz, and the mutual influence of their electron orbits is less. A smaller increase of temperature (to 117° C.) is therefore sufficient to break up the interlocking which is characteristic of low-tridymite and convert it into the type which is characteristic of the high-form. The high-form itself, however, has two modifications, an upper and a lower, with an inversion at 163°. This 163° change gives a very small heat-effect, and is probably only a final step in completion of a principal change which occurred at 117°. An explanation for it may be found in the fact that from the high-tridymite structure previously described there may be derived *two* kinds of association of oxygen atoms, since the radial distance between oxygens is nearly but not quite the same as their axial distance, while in quartz the oxygens are definitely associated in pairs. But not enough is known of the symmetry and other properties of low-tridymite, or of the differences between the

[22] J. R. Ashworth, The theory of the intrinsic field of a magnet and the relation of its magnetic to its characteristic electric and thermal properties, *Phil. Mag.*, **43**, 401–419, 1922.

upper and lower high-tridymites, to warrant the construction of models for the lower forms.

Cristobalite.—Cristobalite exhibits the unusual property, which Fenner was the first to observe in silica, of a variable inversion temperature. The higher the temperature at which the cristobalite was formed, the higher is its high-low inversion point. The explanation of this property evidently calls for some kind of structure which changes at high temperatures but which is preserved at lower temperatures and is not affected by the inversion. It can be accounted for by assuming that the structure is incomplete as regards the oxygen atoms, only a part of the triplets being held in relatively fixed positions while the others still vibrate or rotate about the axis of the silica thread. Rapid cooling to the neighborhood of 200–300° then preserves this mixed structure.

In low-cristobalite the average distance of oxygen atoms is intermediate between that in quartz and that in tridymite. Its range of inversion temperatures is also intermediate (200–275°). But according to the above hypothesis of its structure, the arrangement of oxygens is not complete, some being in haphazard positions just as they were in the glass from which the cristobalite was derived. Accordingly, the oxygen pairs are variously spaced and not all of them will invert at the same temperature; the inversion curve will be drawn out and rounded off, as has been found experimentally by several investigators. The "inversion-temperature" determined by a time-temperature curve (the method used by Fenner) is therefore only a mean value, or a temperature near which the most of the pairs invert. It will readily be seen that as the proportion of haphazard oxygen-pairs is varied by heating the cristobalite at different high temperatures, the mean inversion-temperature will also vary. The phenomenon is rare among polymorphic substances because few are so slow as silica in attaining structural equilibrium.[23]

[23] The structure proposed for high-cristobalite is perhaps the least satisfactory part of the theory. I know of no facts in opposition to it, but it involves an unusual assumption, namely, that it is possible to have a crystalline substance in which not all the atoms are in geometrically defined positions. With apologies to specialists in phase rule and thermodynamics, it might be crudely called a "solid solution of a glass in a crystal." If later X-ray work on cristobalite should prove this impossible, then some other mixed structure must be found which changes at high temperatures but is preserved by rapid cooling and is unaffected by the inversion.

Silica Glass.—The solid character of silica glass is due primarily to the existence of long silica threads and their entanglement, and only secondarily to the interconnection of oxygen atoms. Externally paired oxygens can doubtless be found, but their distances apart vary continuously over a wide range of values. Accordingly, the high-low inversions in those pairs are scattered over a range of temperatures and no marked effect is discernible at any one temperature.

Chalcedony.—Specimens of chalcedony examined by Hull gave an X-ray pattern which is identical with that of quartz.[24] But Fenner could find no evidence of the 573° quartz inversion in his specimens of chalcedony, and the fact that his material changed partly into quartz and tridymite below 870° also indicated that it could not be the same substance as quartz. If we assume that chalcedony is a submicroscopic fibrous mixture of quartz-threads and amorphous-threads the facts are accounted for. There might be an insufficient number of similarly interconnected oxygen-pairs in such a mixture to give a sharp inversion point, and the amorphous-threads would not give any pattern on the X-ray plate, although the quartz-threads would, if grouped in units having a diameter of the order of magnitude of colloid particles. Other facts, such as ease of conversion to cristobalite, are also consistently explained. Slightly different arrangements of the quartz-thread groups without actually interconnecting them, together with the presence of variable small amounts of water between the threads, will probably suffice to account for the variable optical properties which have led mineralogists to distinguish between certain varieties known as quartzine, lutecite, etc.

At the same time it is important to remark that the name "chalcedony" may cover a number of distinct substances, and comparative results on the *same specimen* are much needed.

EXTENSION TO SILICATE SYSTEMS.

If the foregoing hypotheses are true as regards the self-containedness of the SiO_2 triplet, its association into threads, its threefold upbuilding into crystalline modifications, and the intimate nature of its high-low inversions, then they should be capable of extension into the theory of systems of which silica

[24] Washburn and Navias, *Proc. Nat. Acad. Sci.*, **8**, 1–5, 1922.

is a component. There is not space here to take up such an extension in any detail, and I shall indicate only a few scattered applications. In the system $SiO_2 : H_2O$ the thread hypothesis seems capable of accounting for some of the properties of colloidal silica. A stiff silica gel, for instance, may be pictured as something like a wad of cotton saturated with water.

The polymorphism of the silicates offers many interesting suggestions. The 1:1 aluminum silicate, Al_2SiO_5 or $Al_2O_3 \cdot SiO_2$, shows the following parallel with silica in density and stability:

	SiO_2	$Al_2O_3 \cdot SiO_2$
Densest form, unstable at high temperatures:	Quartz	Kyanite
Stable high-temperature form, intermediate in density:	Cristobalite	Sillimanite
Lightest form, nearly same density as stable form:	Tridymite	Andalusite

The threefold sluggish-type polymorphism of silica is again duplicated in the three forms of the potash feldspar ($KAlSi_3O_8$) and possibly in soda feldspar ($NaAlSi_3O_8$), magnesium metasilicate ($MgSiO_3$), and other silicates. The negative expansion coefficient of high-quartz appears in two of the axes of the highly siliceous soda and potash feldspars (Fizeau.) The high-low inversion curve of quartz is duplicated in detail by a similar high-low inversion in leucite at a slightly higher temperature. And so on. These are scattered examples among the silicates of phenomena whose explanation must take into account the theory of polymorphism of silica itself.

ANALOGIES WITH OTHER ELEMENTS OF GROUP IV.

The foregoing hypotheses have been based in part upon an atomic structure for silicon containing 4 "outside" electrons, or 4 electrons in a group having orbits of the highest quantum number. We must expect then that other elements having a similar external structure will show similar chemical phenomena.

There are some suggestive analogies between the properties of silica and those of the dioxides of the other tetravalent elements close to silicon in the Periodic System. The four oxides, TiO_2, GeO_2, ZrO_2, and SnO_2, are all solid oxides of high melting point, which combine with water to form colloidal hydrates and

with basic oxides to form solid compounds (titanates, germanates, zirconates, stannates) showing many resemblances to the silicates. The analogies in their polymorphism are equally suggestive. TiO_2, the best known of the four, exists in three polymorphic forms, each of which has a temperature-range of stability, like the three forms of SiO_2. SnO_2, likewise, exists in three forms,[25] which appear to be isotrimorphous with the forms of TiO_2, but whose properties have not been determined with certainty. Much less is known of ZrO_2, of which two forms are on record; while GeO_2 has scarcely been studied at all and the desired data are wholly lacking. High-low inversions occur in all three forms of TiO_2 and in the cassiterite form of SnO_2, as is revealed by specific heat determinations.[26] Further search for such inversions in all the dioxides mentioned should yield results of interest.

SUMMARY.

There exists a wide variety of experimental data on the forms of silica, and particularly on quartz, which have never been assembled and explained on the basis of a single consistent set of hypotheses as to the ultimate structure of this substance. This paper attempts to provide such a set of hypotheses, based upon the general knowledge already gained concerning the structure of matter in general and silica in particular.

It is believed that the silica atom-triplet maintains a certain degree of individuality in its amorphous and crystalline states as well as in its compounds, and the freedom of its oxygen atoms to change their positions with respect to the silicons is restricted. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure persists in the crystalline states. The three principal crystalline modifications (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in three different ways, the connection between threads being through the oxygen atoms. The high-low ($\alpha - \beta$) inversions in all the forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electron orbits, resulting from increased thermal vibra-

[25] Wunder, *J. prakt. Chem.*, **2**, 206–212, 1870.

[26] Lashchenko, *Bull. Inst. Polyt. Don*, **2**, 8–46, 1913.

tion of the atoms, whereby the shape of the silica triplet and the relative positions of the two oxygen atoms are suddenly altered.

The theory as a whole gives a satisfactory explanation for many phenomena of silica not discussed in this paper, such as the minimum in the temperature-volume curve of silica glass, the relations between the specific heats of the crystalline forms, the effect of surface and of twinning on the conversion of quartz into cristobalite, the fact that natural quartz formed at a high temperature is always homogeneous, while low-temperature vein-quartz is right- and left-twinned, etc. Further, many phenomena not yet tested experimentally are predictable from the theory. I hope to take up these matters in more detail in a book on the properties of silica, which is now in preparation.

CORRECTION.

THE APPLICATION OF THERMODYNAMICS TO HETEROGENEOUS EQUILIBRIA.

BY

GEORGE W. MOREY,

Physical Chemist, Geophysical Laboratory, Washington, D.C.

(JOURNAL OF THE FRANKLIN INSTITUTE, October, 1922, page 425.)

Page 455, line 8, parenthesis in equation should read $(1-x)$.

Page 463, last 4 lines should be omitted, beginning with "Fig. 7 shows" etc.

Page 480, 4th line from bottom, equation should read:

$$\frac{\delta \mu}{\delta T} = -\frac{\delta S}{\delta m_1} = -\bar{s}_1$$

Determination of the External Magnetic Field of the Sun from the Structure of the Corona of the Sun and the Constants of the Aurora Borealis. CARL STORMER. (*Comptes Rendus*, June 6, 1922.)—The author makes use of results coming from his expedition to Bossekop in 1913 to calculate the strength of the external magnetic field of the sun. At its equatorial surface this amounts to $.6 \times 10^{-7}$ gausses, while at its polar surface the value is twice as much. These are of the same order of magnitude as those obtained by Deslandres in 1911, but they are notably smaller than the strength of field found, on the basis of the Zeeman effect, by Hale for regions within the solar atmosphere.

The assumption is made that the same corpuscles are in evidence both in the auroral streamers and in the aurora borealis.

G. F. S.

THE HEAVISIDE EXPANSION THEOREM.*

BY

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HEAVISIDE formulated a theorem, known as his "Expansion Theorem," [1] which is of great utility in the solution of many electrical problems. By the aid of this theorem the current distribution in any network of circuits, the steady state, as well as the transient state, is readily obtained. The theorem is of course of greatest importance in the determination of transient effects which by the usual methods is at best a laborious process, the difficulties increasing as the number of degrees of freedom of the system increases. The reason, perhaps, that this important theorem is not as widely known and as extensively used as its merits deserve may be due to the fact that the derivation of it as given by Heaviside offers difficulties for the engineer and physicist to follow, and its importance was therefore not fully appreciated.

The following simple derivation of the theorem making use of the Heaviside expansion methods will, it is hoped, create a greater interest in the application of this theorem to the solution of electrical problems. The derivation of the theorem is worked out for two cases; a constant electromotive force, and a sinusoidal electromotive force.

The problem may be stated as follows: Given any network of circuits and an e.m.f. applied at any point in the system, what is the current at any time, t, after the electromotive force is applied?

CONSTANT E.M.F.

We may write

$$I = \frac{E}{Z(p)} \qquad (1)$$

* Communicated by General George O. Squier, Chief Signal Officer, U.S.A., and Associate Editor of this JOURNAL.

[1] "Oliver Heaviside Collected Papers," Vol. 2, p. 371, and "Electromagnetic Theory," Vol. 2, p. 127. See also J. R. Carson, *Physical Review*, 10, p. 217, and "The Theory of the Submarine Telegraph and Telephone Cable," Chap. 9, by H. W. Malcolm.

Where $Z(p)$ is the generalized impedance and $p = \frac{d}{dt}$ the time differential. $Z(p)$ may be an expression of any degree in p. We may put

$$Z(p) = (p-p_1)(p-p_2)(p-p_3) \ldots\ldots (p-p_m), \tag{2}$$

where $p_1, p_2 \ldots\ldots p_m$ are the roots of the equation

$$Z(p) = o. \tag{3}$$

By the use of partial fractions, we may put $\frac{1}{Z(p)}$ in the following form:

$$\frac{1}{Z(p)} = \frac{1}{(p-p_1)(p-p_2)(p-p_3)\ldots(p-p_m)} = \frac{A}{p-p_1} + \frac{B}{p-p_2} + \frac{C}{p-p_3} + \ldots\ldots \frac{M}{p-p_m}. \tag{4}$$

The constants $A, B, C, \ldots\ldots M$ are determined in the usual way

$$\left.\begin{aligned} A &= \frac{1}{(p_1-p_2)(p_1-p_3)\ldots\ldots(p_1-p_m)} \\ B &= \frac{1}{(p_2-p_1)(p_2-p_3)\ldots\ldots(p_2-p_m)} \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ M &= \frac{1}{(p_m-p_1)(p_m-p_2)\ldots\ldots p_m-p_{m-1}} \end{aligned}\right\} \tag{5}$$

The following notation is convenient:

$$\left.\begin{aligned} A &= \frac{1}{Z(p_1)} \\ B &= \frac{1}{Z(p_2)} \\ &\cdots\cdots \\ M &= \frac{1}{Z(p_m)} \end{aligned}\right\} \tag{6}$$

Substituting in (1), we get

$$I = E\left\{\frac{1}{(p-p_1)Z(p_1)} + \frac{1}{(p-p_2)Z(p_2)} + \ldots\ldots \frac{M}{(p-p_m)Z(p_m)}\right\} \tag{7}$$

Expanding the term $\frac{1}{p-p_1}$ we have

$$\frac{1}{p-p_1} = \frac{1}{p}\left\{1 - \frac{p_1}{p}\right\}^{-1} = \frac{1}{p}\left\{1 + \frac{p_1}{p} + \frac{p_1^2}{p^2} + \frac{p_1^3}{p^3} + \ldots\ldots\right\} \tag{8}$$

Operating on unity by $\frac{1}{p}$ which means integration with respect to t, we get

$$\frac{1}{p-p_1} = \frac{1}{p}\left\{1 + p_1 t + \frac{p_1^2 t^2}{\underline{|2}} + \frac{p_1^3 t^3}{\underline{|3}} + \cdots\cdots\right\} \tag{9}$$

$$= \frac{1}{p}\, \epsilon^{p_1 t}$$

Operating on $\epsilon^{p_1 t}$ by $\frac{1}{p}$ we obtain

$$\frac{1}{p-p_1} = \frac{1}{p}\, \epsilon^{p_1 t} = \int_0^t \epsilon^{p_1 t} dt = \frac{1}{p_1}\, \epsilon^{p_1 t}\Big]_0^t = \frac{1}{p_1}\left[\epsilon^{p_1 t} - 1\right]. \tag{10}$$

Applying the same process to each of the terms in equation (7), we finally get

$$1 = E\left\{\frac{\epsilon^{p_1 t}}{p_1 Z(p_1)} + \frac{\epsilon^{p_2 t}}{p_2 Z(p_2)} + \cdots\cdots \frac{\epsilon^{p_m t}}{p_m Z(p_m)} - \frac{1}{p_1 Z(p_1)} - \frac{1}{p_2 Z(p_2)} - \cdots\cdots \frac{1}{p_m Z(p_m)}\right\}. \tag{11}$$

The above expression may be simplified in the following manner. Put

$$Z(p) = (p-p_1)\, F(p)$$

$$\frac{\partial Z(p)}{\partial p} = (p-p_1)\, \frac{\partial F(p)}{\partial p} + F(p)$$

$$F(p) = (p-p_2)\,(p-p_3)\,(p-p_4)\cdots\cdots\,(p-p_m)$$

For $p = p_1$ by (5)

$$\frac{\partial Z(p)}{\partial p}_{p=p_1} = F(p)_{p=p_1} = (p_1-p_2)\,(p_1-p_3)\cdots\cdots = Z(p_1) \tag{12}$$

Similarly for the denominators in the other terms of (11),

$$\left.\begin{aligned} Z(p_2) &= \frac{\partial Z(p)}{\partial p}_{p=p_2} \\ Z(p_3) &= \frac{\partial Z(p)}{\partial p}_{p=p_3} \\ &\cdots\cdots\cdots \\ Z(p_m) &= \frac{\partial Z(p)}{\partial p}_{p=p_m} \end{aligned}\right\} \tag{13}$$

Also if we put $p = 0$ in (4) we get

$$\frac{1}{Z(p)_{p=0}} = -\left\{\frac{1}{p_1 Z(p_1)} + \frac{1}{p_2 Z(p_2)} + \cdots \frac{1}{p_m Z(p_m)}\cdot\right\} \tag{14}$$

Substituting from (12), (13) and (14) in (11) we get the final formula

$$I = \frac{E}{Z(p)_{p=0}} + E\left\{\frac{\epsilon^{p_1 t}}{p_1 \dfrac{\partial Z(p)}{\partial p}_{p=1}} + \frac{\epsilon^{p_2 t}}{p_2 \dfrac{\partial Z(p)}{\partial p}_{p=2}} + \cdots\right\}$$

$$= \frac{E}{Z(p)_{p=o}} + \sum_{n=1}^{n=m} \frac{E\varepsilon^{p_n t}}{\frac{\partial Z(p)}{\partial p}_{p=p_n}} \qquad (15)$$

Equation (15) is the form in which Heaviside gave the theorem in his "Electromagnetic Theory" (Vol. 2, page 127). $Z(p)_{p=o}$ is the algebraic function obtained by putting $p=o$ in $Z(p)$. It is the effective steady resistance to E. The term $\frac{\partial Z(p)}{\partial p}$ is the ordinary differential coefficient of Z with respect to p as a quantity and the summation to be extended to all the roots of the algebraic equation $Z(p)=O$. The summation term of equation (15) represents the transient current in system. Several illustrations of the application of this formula to the solution of electrical problems are given by Heaviside.

SINUSOIDAL E.M.F.

If the impressed e.m.f. is sinusoidal, of frequency $\frac{w}{2\pi}$, we can write

$$e = E\varepsilon^{jwt}$$

For brevity, put $jw=\lambda$, we have as in equation (1)

$$I = \frac{E\varepsilon^{\lambda t}}{Z(p)} \qquad (16)$$

$$I = E\left\{\frac{1}{(p-p_1)\,Z\,(p_1)} + \frac{1}{(p-p_2)\,Z\,(p_2)} + \cdots \frac{1}{(p-p_m)\,Z\,(p_m)}\right\}\varepsilon^{\lambda t} \qquad (17)$$

Operating by $\frac{1}{p}$ on the function $\varepsilon^{\lambda t}$, we have

$$\frac{1}{p}\varepsilon^{\lambda t} = \int_o^t \varepsilon^{\lambda t}\,dt = \frac{1}{\lambda}\varepsilon^{\lambda t} - \frac{1}{\lambda}$$

$$\frac{1}{p^2}\varepsilon^{\lambda t} = \int_o^t \left(\frac{1}{\lambda}\varepsilon^{\lambda t} - \frac{1}{\lambda}\right)dt = \frac{1}{\lambda^2}\varepsilon^{\lambda t} - \frac{1}{\lambda^2} - \frac{1}{\lambda}t$$

$$\frac{1}{p^3}\varepsilon^{\lambda t} = \int_o^t \left(\frac{1}{\lambda^2}\varepsilon^{\lambda t} - \frac{1}{\lambda^2} - \frac{1}{\lambda}t\right)dt = \frac{1}{\lambda^3}\varepsilon^{\lambda t} - \frac{1}{\lambda^2} - \frac{1}{\lambda^2}t - \frac{1}{\lambda}\frac{t^2}{\underline{2}} \qquad (18)$$

Repeating the process over and over, we get

$$\frac{1}{p^m}\varepsilon^{\lambda t} = \frac{1}{\lambda^m}\varepsilon^{\lambda t} - \frac{1}{\lambda^m} - \frac{1}{\lambda^{m-1}}t - \frac{1}{\lambda^{m-2}}\frac{t^2}{\underline{2}} - \frac{1}{\lambda^{m-3}}\frac{t^3}{\underline{3}} - \cdots$$

Expanding the term $\frac{1}{p-p_1}$, the denominator of the first term in (17), as in (8)

$$\frac{1}{p-p_1} = \frac{1}{p}\left(1 + \frac{p_1}{p} + \frac{p_1^2}{p^2} + \frac{p_1^3}{p^3} + \cdots\right\}$$

Operating on $\epsilon^{\lambda t}$ and using the values given in (18) we get

$$\begin{aligned}\frac{1}{p-p_1}\epsilon^{\lambda t} = \frac{1}{p}\Big\{ & \epsilon^{\lambda_1 t} + \frac{p_1}{\lambda}\epsilon^{\lambda t} - \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2}\epsilon^{\lambda t} - \frac{p_1^2}{\lambda^2} - \frac{p_1^2}{\lambda} t \\ & + \frac{p_1^3}{\lambda^3}\epsilon^{\lambda t} - \frac{p_1^3}{\lambda^3} - \frac{p_1^3}{\lambda^2} t - \frac{p_1^3}{\lambda}\frac{t^2}{\lfloor 2} \\ & + \frac{p_1^4}{\lambda^4}\epsilon^{\lambda t} - \frac{p_1^4}{\lambda^4} - \frac{p_1^4}{\lambda^3} t - \frac{p_1^4}{\lambda^2}\frac{t^2}{\lfloor 2} - \frac{p_1^4}{\lambda}\frac{t^3}{\lfloor 3} \\ & + \cdots\cdots\cdots\cdots\cdots\cdots\end{aligned} \tag{19}$$

Rearranging we get

$$\begin{aligned}\frac{1}{p-p_1}\epsilon^{\lambda t} = \frac{1}{p}\Big\{ & \epsilon^{\lambda t}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\right) - \frac{p_1}{\lambda}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\right) \\ & - \frac{p_1^2}{\lambda} t\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\cdots\right) \\ & - \frac{p_1^2}{\lambda}\frac{t^2}{\lfloor 2}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\cdots\right) \\ & - \cdots\cdots\cdots\cdots\cdots\cdots\end{aligned}$$

The above is equal to

$$\begin{aligned}& \frac{1}{1-\frac{p_1}{\lambda}}\frac{1}{p}\left\{\epsilon^{\lambda t} - \frac{p_1}{\lambda}\left(1 + p_1 t + \frac{p_1^2 t^2}{\lfloor 2} + \frac{p_1^3 t^3}{\lfloor 3} + \cdots\right)\right\} \\ & = \frac{1}{1-\frac{p_1}{\lambda}}\frac{1}{p}\left(\epsilon^{\lambda t} - \frac{p_1}{\lambda}\epsilon^{p_1 t}\right)\end{aligned}$$

Operating again by $\frac{1}{p}$, we have finally

$$\frac{1}{p-p_1}\epsilon^{\lambda t} = \frac{1}{\lambda-p_1}\left\{\epsilon^{\lambda t} - \epsilon^{p_1 t}\right\} \tag{20}$$

Extending the same operation to the other terms of (17), we get

$$\begin{aligned}I = & E\epsilon^{\lambda t}\left\{\frac{1}{(\lambda-p_1)Z(p_1)} + \frac{1}{(\lambda-p_2)Z(p_2)} + \cdots\cdots\right\} \\ & - E\left\{\frac{\epsilon^{p_1 t}}{(\lambda-p_1)Z(p_1)} + \frac{\epsilon^{p_2 t}}{(\lambda-p_2)Z(p_2)} + \cdots\cdots\right\}\end{aligned} \tag{21}$$

By putting in equation (4) $p=\lambda$, we have

$$Z(p)_{p=\lambda} = \frac{1}{(\lambda-p_1)\,Z(p_1)} + \frac{1}{(\lambda-p_2)\,Z(p_2)} + \cdots\cdots$$

Substituting this value in (27), we get

$$I = \frac{E\,e^{\lambda t}}{Z(p)_{p=\lambda}} - \sum_{n=1}^{n=m} \frac{e^{p_n t}}{(\lambda-p_n)\,Z(p_n)} \qquad (22)$$

By (13) we have $Z(p_n) = \frac{\partial Z(p)}{\partial p}\,p=p_n$, substituting this in (22), we get for the final expression

$$I = \frac{E\,e^{\lambda t}}{Z(p)_{p=\lambda}} - \sum_{n=1}^{n=m} \frac{e^{p_n t}}{(\lambda-p_n)\,\frac{\partial Z(p)}{\partial p}\,p=p_n} \qquad (23)$$

Here again the first term, replacing λ by jw, represents the permanent state, the current in the system due to an impressed sinusoidal e.m.f. of frequency $\frac{w}{2\pi}$, and the second summation term the transient current before the permanent state is reached.

Determination of the Velocity of Alpha Rays from Polonium. MISS IRENE CURIE. (*Comptes Rendus*, July 24, 1922.)—The polonium employed had been separated from RaD by electrolysis and afterwards deposited on silver foil. The alpha rays emitted by the deposit passed in turn through two narrow slits so that only a sharply defined ray came through the second aperture. Upon the particles forming this ray acted a uniform magnetic field of about 10,000 gausses. Its direction was at right angles to the velocity of the particles. By it the paths of the particles were bent into circles whose radii were got from images recorded on a photographic plate in the presence and again in the absence of the field.

Two series of observations lead to the same value for the velocity of the alpha particles of polonium, 1.593×10^9 cm. per sec., or about one-sixth of the velocity of light. Alpha rays from polonium, according to Miss Curie's results, have .829 of the velocity of similar particles originating from RaC. The ranges of the two kinds of particles are from other experiments known to be, respectively, 3.925 and 6.971 cm. When Geiger's law that the ranges are in proportion to the cubes of the velocities is applied, the corresponding ratio of the velocities comes out equal to .826.

The frequent contributions of the present Lord Rayleigh to the literature of physics, the recent election of Captain Thomson, the son of Sir J. J. Thomson, to the chair of Natural Philosophy at Aberdeen and the work of Miss Curie in the field of radioactivity will furnish data for a study of the transmissibility of the acquired characteristic of ability in investigation. G. F. S.

BIOCHEMICAL OBSERVATIONS ON CERTAIN INSECTIVOROUS PLANTS.*

BY

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NEPENTHES AND ITS PITCHER LIQUOR.

THE *Nepenthaceæ*, or East Indian family of pitcher plants, consists of a single genus *Nepenthes* which includes a number of species. In the *Nepenthes*, the midrib is prolonged beyond the blade of the leaf as a tendril. The end of this tendril becomes evaginated or bulged to form a pitcher and its operculum or lid. As the pitcher and lid develop, they enclose a hermetically sealed space, the pitcher cavity, into which a liquor is secreted. Finally, when the pitcher has attained the proper stage of development, the lid opens and remains permanently in the open position.

After the lid has opened, insects are attracted by the nectar which is secreted by glands. These nectar glands occur on the outer surface of the pitcher, but are more abundant on the inner surface of the lid and on the inner edge of the corrugated rim that surrounds the top of the pitcher. The insects, which are attracted, are thus tempted downward into the pitcher, and pass to a richly glandular zone with a smooth surface—the so-called detentive surface. Here they lose their footing and fall into the pitcher liquor. The insects are then digested by the liquor.

Experimental evidence of the secretion of a proteolytic enzyme by the pitchers has been presented by Hooker,[1, 2] Tait,[3] von Gorup and Will,[4, 5] Vines,[6, 7, 8, 9, 10] Goebel,[11] Clautriau,[12] Fenner,[13] and Abderhalden and Teruuchi.[14] Other investigators—Tischutkin,[15, 16] Dubois,[17, 18] Couvreur,[19, 20] and Clément[21]—have deduced from their researches that the pitcher liquor does not contain a protease secreted by the plant, and that the digestion is due to bacterial action. Tests for the presence of enzymes, other than protease, have been made by comparatively few investigators. Tests for diastase were made by von Gorup and Will,[4, 5] by Vines,[6] and by Robinson;[22] the results were entirely negative.

* Communicated by the Author.

Robinson [22] also tested for the presence of invertase, lipase and esterase, likewise with negative results.

The action of rattlesnake venom upon *Nepenthes* has been studied by John Marshall of the Robert Hare Laboratory of Chemistry at the University of Pennsylvania. In a personal communication to the author, dated March 29, 1920, Doctor Marshall states: "About twelve years ago I placed some rattlesnake venom in the pitchers of some *Nepenthes* in our botanical garden and found that nothing harmful resulted to the plant. I also injected some fresh venom into the tissue of the stalk of *Nepenthes* with no observable harmful effects upon the plant."

In previous communications,[23, 24] the author has described an extensive series of experiments concerning the presence of a protease in the liquor obtained from pitchers entirely free from insect captures. The liquor digested various proteins (edestan, carmine fibrin, protean of castor bean globulin, Jacoby's ricin) in the presence of dilute acid and a bactericide. Hence a protease was present. St. John and the author [25] found that the liquor of closed pitchers is bacteriologically sterile, while that of open active pitchers contains proteolytic bacteria; however, the digestion of proteins by these bacteria was an exceedingly slow process. The conclusion was drawn that the leading rôle in the digestion of the prey is played by the protease of the pitcher liquor, and that bacteria play but a secondary part in the digestion. The tissue enzymes of the captured insects may produce autolysis of their tissues, and thereby assist in the digestion.

The study has been extended to include tests for the presence of the following enzymes in the pitcher liquor: Catalase, urease, esterase, diastase, and the inverting enzymes (invertase, maltase, lactase, and emulsin). The liquor was obtained by means of a hypodermic needle and syringe from closed pitchers of plants growing in the Nepenthes House of the University of Pennsylvania. The needle was passed through the wall of the pitcher above the level of the liquor, then was pushed into the liquor which was immediately drawn into the barrel of the syringe. The tests for the presence of enzymes were begun immediately after the collection of the pitcher liquor.

In each test a blank or control experiment was made, using pitcher liquor which had been boiled to inactivate enzymes, then cooled to the temperature of the laboratory. In all other respects,

each control was a duplicate of its determination proper. Trikresol was used as a bactericide in all the tests except that for catalase. The concentration of the trikresol in each reaction mixture was 0.2 per cent. Unless otherwise stated, the tem-

View in Nepenthes House, Kew Gardens, England.

perature of incubation was 37.5° C., and the period of incubation eight days.

Catalase.—The pitcher liquor (2.5 c.c.) was placed in a test tube four inches in length, which was then filled with a 0.3 molar aqueous solution of hydrogen peroxide. The contents of the tube were well mixed; and the tube was then inverted over a pneumatic trough. At the end of one hour at room temperature, no oxygen gas had collected, hence catalase was absent.

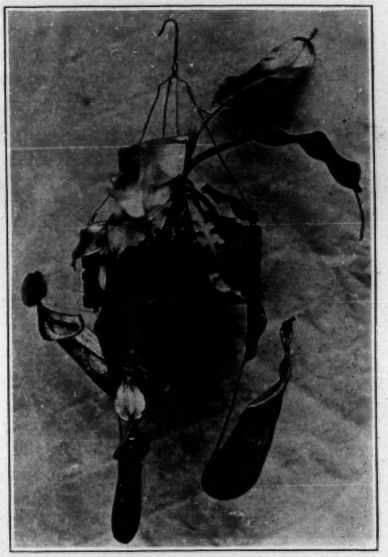
Urease.—The pitcher liquor (5 c.c.) was mixed with an equal volume of a 1 per cent. aqueous solution of urea. After incubation, the determination proper and the control each required 0.20 c.c. of 0.1 normal sulphuric acid to render them neutral to methyl orange. Since the alkalinity of the determination proper did not exceed that of the control, the urea had not been cleaved by urease, and that enzyme was not present in the pitcher liquor.

Esterase.—The pitcher liquor (6.25 c.c.) was mixed with 4 c.c. of distilled water and 1 c.c. of ethyl butyrate. After the addition of the bactericide, both the determination proper and the control were rendered neutral to phenolphthalein by addition of 0.1 normal sodium hydroxide solution. After incubation, both the determination proper and the control required 0.05 c.c. of 0.1 normal sodium hydroxide solution to restore their reaction to the neutral point. Since the acidity of the determination proper did not exceed that of the control, enzymic cleavage of the ethyl butyrate had not occurred, and esterase was not present in the pitcher liquor. The absence of esterase would indicate the absence of lipase also, since these two enzymes are closely related, if not identical.

Diastase.—The pitcher liquor used in the test for this enzyme did not reduce Benedict qualitative alkaline copper solution; 4 c.c. of the liquor were mixed with an equal volume of a 1 per cent. aqueous solution of soluble starch. After incubation, both the determination proper and the control yielded the blue color of starch iodide with Lugol solution (iodine dissolved in an aqueous solution of potassium iodide), and both had absolutely no reducing action on the Benedict solution. Therefore, the starch had not been hydrolyzed, and diastase (amylase) was not present in the pitcher liquor.

Inverting Enzymes.—Preliminary tests showed that the pitcher liquor used in this series of experiments had no action on Benedict qualitative alkaline copper solution, and therefore did not contain reducing sugar. In each test for the presence of an inverting enzyme, 4 c.c. of the pitcher liquor were mixed with an equal volume of a 1 per cent. aqueous solution of the proper substrate, *i.e.*, sucrose for invertase, α-methyl *d*-glucoside for maltase, lactose for lactase, and amygdalin for emulsin. In the tests for invertase, maltase, and emulsin, after incubation, both the determination proper and its blank were permitted to act upon

the Benedict solution. However, lactose reduces Benedict solution; therefore, in the test for lactase after incubation, both the determination proper and its blank were permitted to react with Barfoed solution at the temperature of boiling water for a period of twenty-five minutes. Barfoed solution (an aqueous solution of cupric acetate rendered acid with acetic acid) is not reduced



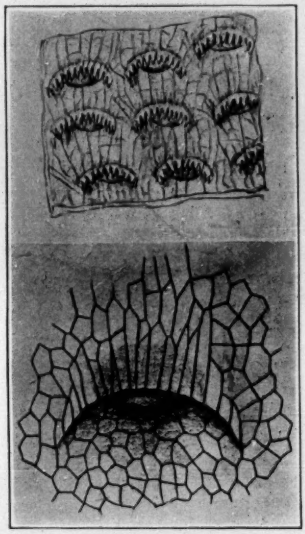
Nepenthes Dyeriana, showing the blade, the tendril, and the open pitcher of each leaf.

under these conditions by the disaccharides including lactose, but is reduced by their cleavage products, the monosaccharides.

In the test for each of the four enzymes, neither the determination proper nor its blank reduced the copper solution; therefore, the inverting enzymes were not present in the pitcher liquor.

The presence of a protease in the pitcher liquor, and the absence of enzymes acting upon carbohydrates and fats, are evidence that the liquor is secreted in order to digest the proteins in the bodies of the captured insects, and thereby to supply the plant with nitrogenous food.

The pitcher plants include three families, subdivided into five genera. The family *Nepenthaceæ* contains one genus *Nepenthes;* the family *Cephalotaceæ,* one genus *Cephalotus;* and the family *Sarraceniaceæ,* three genera, *Heliamphora, Darlingtonia,* and *Sarracenia.* In another communication,[26] we have reviewed the work of previous investigators, and have described our own experiments which showed the presence of a protease in the pitcher liquor of six species of the genus *Sarracenia* and its absence from that of *Darlingtonia californica,* the only species of that genus. The most recent work of this nature on the genus *Cephalotus* is that of Dakin;[27] he has found a protease in the pitcher liquor of *Cephalotus follicularis,* the only species of that genus. Therefore, it may be concluded on both morphological and biochemical grounds that the pitchers of most, if not all, species of pitcher plants are designed for the capture and digestion of prey as a means of nutrition for the plant.



Digestive glands of *Nepenthes,* each inbedded underneath a projecting pocket-like flap. A group of the glands is shown in the upper section, a single gland at a higher magnification in the lower section.

Presence of Reducing Sugar.—The samples of pitcher liquor used in the tests for diastase and the inverting enzymes did not reduce Benedict qualitative alkaline copper solution. However, the liquor may at times reduce that solution. Twelve composite samples of liquor were collected from closed pitchers or from pitchers which had recently opened and were free from insects; nine of these samples reduced the Benedict solution, the other three samples had no action on that reagent. The type of pitcher, closed or open, had no influence on the response to this test. When reduction occurred, it was probably due to the presence of sugar derived from the nectar.

Tests for Anions.—A composite sample of liquor from closed pitchers was tested for the presence of chlorides and phosphates. It yielded a white curdy precipitate with silver nitrate solution. This precipitate was soluble in ammonia water, and was reprecipitated from the resulting solution on addition of nitric acid. Therefore chlorides were present. The liquor was digested with ammonium molybdate in the presence of nitric acid; a precipitate was not formed; therefore phosphates were absent. These results are in harmony with those obtained by Voelcker [28] in testing for these two acid radicals.

Test for Saponins.—According to Clautriau,[12] the pitcher liquor contains in solution a substance which causes insects to become wet and to sink. Saponins would confer this property upon the pitcher liquor if present in it, since they lower the surface tension. The hæmolysis test for saponins was therefore applied to liquor freshly collected from closed pitchers. The finger was pricked and blood was permitted to fall into 0.5 c.c. of a 0.1 per cent. solution of sodium citrate in a physiological (0.85 per cent.) solution of sodium chloride, until the volume of the latter had doubled. Equal volumes of the resulting suspension of human erythrocytes and the pitcher liquor were mixed on a glass slide, covered with a glass slip, and then examined through a microscope. The erythrocytes, or red corpuscles, remained intact at the end of thirty minutes; therefore hæmolysis did not occur, and saponins were absent from the pitcher liquor. In a control experiment, a dilute aqueous solution of digitonin, a saponin, was substituted for the pitcher liquor; complete hæmolysis occurred immediately.

DIONÆA MUSCIPULA.

The Venus fly trap, *Dionæa muscipula,* is an insectivorous plant, whose native habitat is in eastern North Carolina. It is the only species of the genus *Dionæa* which belongs to the family *Drosceraceæ.* Therefore the Venus fly trap is closely related to the sun dews. In this plant, a foliaceous footstalk supports a bilobed leaf which is provided with a margin of spikes. Several trigger hairs, usually three, are present on the upper surface of each lobe. In the open leaf, the two lobes are at slightly less than a right angle to each other. When an insect comes upon the leaf, it may touch one of the trigger hairs, but nothing happens. As

the insect moves about the leaf, it may touch the same trigger hair a second time, or it may touch another trigger hair. In either case, upon the second contact, the leaf snaps shut upon the insect.[31] The two lobes close, the midrib serving as a fulcrum; and the spikes interlock. A fluid is secreted; and the insect undergoes digestion. When digestion and absorption of its products are complete, the leaf again opens. Darwin[29] describes his own experiments on this plant, and also cites the work of others in his treatise on Insectivorous Plants.

Frank Morton Jones, of Wilmington, Delaware, collected

Dionæa muscipula in its native habitat near Wilmington, North Carolina, showing both open and closed leaves. A leaf in the foreground has opened, but still contains the indigestible residue of its prey. Photograph taken by Charles W. Palmer and Walter Steckbeck, July 1, 1917.

both the secretion and the leaves from plants of *Dionæa muscipula* growing in their native habitat near Wilmington, North Carolina, at the end of the month of May, and presented them to the author for biochemical study.

The *secretion* was a composite sample gathered by means of a small pipette from fifty closed leaves containing captured insects. It was a glairy liquid, and was tested for the presence of a proteolytic enzyme. In one experiment, 0.3 c.c. of the secretion and 0.2 gram of carmine fibrin were added to 20 c.c. of an aqueous solution containing 0.2 per cent. hydrochloric acid and 0.2 per cent. trikresol; the carmine fibrin was completely dissolved

on digestion for six days at the temperature of the laboratory. In another experiment, 0.3 c.c. of the secretion and 0.2 gram of carmine fibrin were added to 20 c.c. of an aqueous solution containing 0.5 per cent. sodium carbonate and 0.2 per cent. trikresol. The carmine fibrin was not even attacked during digestion for six days at the temperature of the laboratory. The proper control or blank experiments were also made, and showed no digestion of the substrate. These results indicate the secretion by the leaves of a protease which is active in the presence of a dilute acid. This protease doubtless digests proteins in the bodies of the captured insects, and thereby makes them available for absorption and the nutrition of the plant.

The entire *leaves* had been thoroughly washed in running cold water to remove the secretion, prey, and any foreign matter, and had been permitted to become air-dried. They were ground until the entire mass passed through a sieve with twenty meshes to the linear inch. This mass, which represented a composite sample of fifty or more leaves, was used for chemical analysis according to the methods of the Association of Official Agricultural Chemists.[30] The results are recorded in Table I. Crude fat is a

TABLE I.

Percentage Composition of the Leaves of Dionæa Muscipula.

Constituent.	Air-dried Leaves.	Calculated on Water-free Basis.
Moisture	8.38	....
Total solids	91.62	100.00
Crude protein	8.31	9.07
Crude fat	11.18	12.20
Crude fibre	11.58	12.64
Nitrogen-free extractives	55.53	60.61
Total ash	5.02	5.48
Insoluble ash	3.32	3.62
Soluble ash	1.70	1.86

synonym for ether extract. The soluble ash is that portion of the total ash which dissolved in boiling water, while the insoluble ash is the portion which was insoluble in that solvent; approximately one-third of the total ash was soluble. The alkalinity of the ash was also determined. The soluble ash present in 1 gram of the air-dried sample required 1.45 c.c. of 0.1 normal hydrochloric acid for its neutralization, while the insoluble ash required 6.14 c.c. These results were recalculated for the total solids; the solu-

ble ash present in 1 gram of total solids required 1.58 c.c. of 0.1 normal hydrochloric acid for its neutralization, while the insoluble ash required 6.70 c.c. Methyl orange was used as an indicator in these titrations.

SUMMARY.

The liquor from pitchers of *Nepenthes*, which were entirely free from insect captures, contained a protease which exerted its activity in a slightly acid medium. Catalase, urease, esterase, diastase, invertase, maltase, lactase, and emulsin were not present in the pitcher liquor.

A substance, which reduced Benedict alkaline copper solution, was frequently, but not invariably, present in the pitcher liquor; it was probably sugar derived from the nectar.

The pitcher liquor contained chlorides, and did not contain phosphates and saponins.

A composite sample of the secretion of the leaves of *Dionæa muscipula* was examined, and was found to contain a protease which was active in the presence of 0.2 per cent. hydrochloric acid.

The leaves of *Dionæa muscipula* have been analyzed; and their composition is reported.

The author is indebted to Dr. Walter Steckbeck for the photograph of *Dionæa muscipula* and to Dr. John M. Macfarlane for those of *Nepenthes*.

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PHILADELPHIA, PA.

The Production of Nitric Oxides and Ozone by High Voltage Electric Discharges.—In Bulletin 9 recently issued by Purdue University, KARL B. MCEACHRON and R. H. GEORGE give in much detail the results of experiments made at the University during the war and somewhat later, to determine conditions which promote the fixation of nitrogen with oxygen, a problem of great importance in industrial

chemistry. It was found that methods for absorption of the gas could be devised which are much simpler than those heretofore in use, and that the amount of equipment was much less. Ozone was produced in almost all the experiments and the data in regard to it have been included. The pamphlet covers 190 pages, including a good index and many diagrams and illustrations.

Some of the conclusions are as follows: Using fresh dry air on Siemens type of tubes, the application of a sufficiently high potential from either an induction coil or a high voltage transformer, will cause a decrease in pressure (the experiment being made with a closed volume of air) which shows a contraction of volume. After reaching a certain point, however, the action reverses, a result that had already been noted by Spiel.

1. Holding conditions as constant as possible the reversal points on check runs do not agree closely with respect to either time or reversal or the amount of pressure decrease. The yield of nitric acid is always much greater near the reversal point than after the pressure has increased up to the initial.

2. In case the air in the tube has been in contact for a considerable time with other air, even in minute quantities, which has been previously subjected to electrical discharge, the pressure decrease is modified or may be eliminated altogether, the pressure rising instead of falling. Such contamination decreases the yield and may under certain conditions prevent the formation of any absorbable products. The appearance of the discharge is greatly modified by such contamination.

3. It was found that the pressure decrease is not proportional to the nitric oxides absorbed. It has not been possible in most cases to account for more than a fractional part of the pressure decrease on the basis of the amount of ozone and nitric acid found. This seems to indicate the presence of some heavy molecule, which is not being absorbed.

4. As a rule the pressure did not decrease more than 60 mm. below the initial pressure, but in one case the decrease was 114 mm., the pressure characteristic being almost a straight line. It has not been possible to duplicate this run. The yield at a point near reversal was much less than that obtained from other runs with a decrease of pressure of not over 30 mm. When taking the probable temperature of the gas into account, the contraction in this run amounts to nearly one-fifth by volume.

5. Alternating current seems in most cases to cause a more rapid pressure decrease than does current from an induction coil having approximately the same effective value. This condition is most pronounced when the time of exposure is relatively short.

H. L.

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, Ph.D.

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54. THE DISCOVERY OF THE ISOTOPES OF NEON.

In 1906 Boltwood of Yale discovered a new radioactive element which he called ionium.[70] This exhibited chemical properties similar to thorium, and is so much like the later that Marckwald and Keetman of Berlin were unable to obtain the slightest detectable separation of the two elements in experiments which involved years of labor.[71] A number of other "isotopic radioactive elements" were discovered in the years which followed, but the first experimental indication of the possible existence of isotopes, among the non-radioactive elements, was obtained by Sir J. J. Thomson, of Cambridge, as described in his address to the Royal Institution on Friday, January 17, 1913, in which he says:

"I now turn to the photograph of the lighter constituents; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

"The origin of this line presents many points of interest: There are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeleef's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the

* Continued from page 681, vol. 194, November, 1922.

[70] Boltwood: *Am. J. Sci.*, **22**, 537 (1906), **24**, 370 (1907).

[71] Keetman: *Jahr. Radioactivität*, **6**, 269 (1909).

sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, although no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeleef's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt. From the relative intensities of the 22 line and the neon line, we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon."

While the evidence obtained for the existence of two isotopes of neon seems now to have been very good, it is said that for many years Thomson himself remained doubtful of their existence. A letter written on May 5, 1919, by Dr. F. W. Aston, Thomson's former assistant, states: "For my own part, I am fairly confident of the existence of neon and meta-neon, but I do not consider that the results so far warrant a definite statement to the public. It is a pity that several authors of text-books seem to have jumped to the conclusion that such has been made."

Thomson's results suggested to Aston that it might be possible to separate neon by distillation from charcoal, or by diffusion. The former method gave no separation, but the latter gave light and heavy fractions of different densities. However, the volume of the extreme fractions was so small, only 2 and 3 c.c., that Aston himself was very doubtful of the result,[72] and did not publish the details of his work until many years later. While Aston undoubtedly secured a slight separation of the isotopes, it is possible that a part of the density change was due to impurities, which are very difficult to exclude from such small fractions, particularly in the case of a gas such as neon.

[72] Aston: *Report British Assoc. Adv. Science*, 1913, p. 403.

55. DISCOVERY OF THE ISOTOPES OF CHLORINE BY HARKINS AND BROEKER (ACTUAL SEPARATION BY THE DIFFUSION METHOD), AND BY ASTON (POSITIVE RAY METHOD).

In 1916 Harkins and Turner began experimental work upon the separation of chlorine into isotopes by the diffusion of gaseous chlorine, in order to demonstrate the correctness of the idea of Harkins and Wilson,[73] that the atomic weights of the chemical elements are good evidence of the existence of isotopes in *chlorine, magnesium,* and *neon,* and in most elements of atomic numbers 28 to 82, particularly in those of even atomic number in this range. The beginning of the experimental work on the separation was announced in the *Journal of the American Chemical Society* in 1916. Since there are two atoms of chlorine in Cl_2, the separation of isotopes should be only one-half as fast with this gas as when hydrogen chloride gas is used. Notwithstanding this fact, it was at first thought that the ease of condensation of the chlorine would compensate for the difference. Though slight density changes were obtained by the first set of repeated diffusions, it was difficult to prove that these were not due to impurities. In order to hasten the separation, which had been stopped by the war, Doctor Turner, in the summers of the years 1917 and 1918, and Mr. Liggett, in the year 1917–18, changed to the diffusion of hydrogen chloride gas. While some separation of the isotopes of chlorine was undoubtedly secured, as was proved by later work on the changes of density, no atomic weight determinations were made at this time. In October, 1919, Harkins and Broeker began the diffusion of HCl gas in the apparatus made by Doctor Turner, and, *in January, 1920, 10 grams of hydrogen chloride, the chlorine of which showed an atomic weight of 35.515, had been obtained,* together with a considerable quantity of the gas containing chlorine of a lower atomic weight than that of the ordinary element. Five atomic weight determinations indicated increases of atomic weight over that of normal chlorine, of 0.052, 0.059, 0.057, 0.055, and 0.053 units. A notice of this separation was published in the February number of the *Physical Review,* and in *Science* and *Nature.*[74] While a preliminary notice of Aston's results on the positive ray analysis of chlorine was

[73] *J. Am. Chem. Soc.,* **37**, 1371, 1390 (1915).

[74] *Physical Review,* **15**, 74 (Feb., 1920); *Science,* N. S., **51**, 289–91 (1920); *Nature,* **105**, 230–1 (1920).

published about six weeks [75] before the publication of our separation, it should be recognized that the chemical methods are much slower than the determinations by the positive ray apparatus, so without doubt the writer and his collaborators had separated chlorine into isotopes *before* Aston had obtained their positive ray analysis. In this connection it should be remembered that the idea that chlorine consists of isotopes, and a notice of the beginning of the separation, had both been published by the writer four and one-half years before Aston made any statement in regard to isotopes in chlorine.

The apparatus used in the separation of the heavy chlorine consisted of 12.2 metres of churchwarden pipe stems, contained in glass tubes and boxes, in which the diffusion was carried out, while the three sets of apparatus for the light fraction were smaller. A somewhat similar apparatus will be described in section 58.

Three months after the publication of the notice of the separation of the isotopes of chlorine, the work, which was proceeding with great rapidity, was stopped by the death of Mr. Broeker. No increase in the atomic weight of the heavy fraction had been obtained since January, since the whole endeavor had been put upon enlarging the quantity of material, which, for the heaviest fraction, had risen to 20 grams. *The relative increase in density, 1 part in 645, is by far the largest yet attained for any element, and the quantity of the final fractions is much greater than that secured later in the case of mercury. This was the first investigation, also, in which appreciable amounts of isotopic material were obtained.*

The chlorine used in the atomic weight determinations was highly purified by methods which will be described in a later section. The efficiency of the process was about 60 per cent.; that is about 60 per cent. of the theoretical change of atomic weight was actually obtained. In calculating the separation to be expected, it was necessary to assume the atomic weights for the individual isotopes. In accordance with the assumption of Harkins and Wilson,[76A] the atomic weight of the lower isotope was taken as 35, and corresponding with their idea that the difference in the atomic weights of isotopes is most commonly

[75] *Nature*, Dec. 18, 1919.

[76] *Loc. cit.*, (A) page 1391; (B) pages 1389-90 (1915).

2,[76B] it was supposed that the most probable weight for the heavier isotope would be 37, which agrees with the weight afterward found.

56. SEPARATION OF THE ISOTOPES OF CHLORINE BY HARKINS AND HAYES.

In order to confirm the separation of chlorine into isotopes as obtained by Harkins and Broeker, it seemed advisable to continue the work on the diffusion of hydrogen chloride gas. Due to the fact that Mr. Broeker had, just previous to his death, adopted an improved, but partly unknown, system of labelling the fractions from his diffusion, it was decided to begin with material of the ordinary atomic weight. This was diffused in an apparatus (see section 58), which has a capacity of 1000 litres of HCl gas, at ordinary pressures, per day. In this way 9 g. of atomic weight 35.498 and 90 g. of atomic weight 35.494 were obtained by the summer of 1921. In addition there was prepared 400 g. of atomic weight about 0.02 unit higher and about 4 kilos of about 0.01 unit higher than ordinary chlorine. The atomic weight determinations were made by the method of Harkins and Broeker, and will be described in sections 59 to 65.

57. SEPARATION OF THE ISOTOPES OF CHLORINE BY HARKINS AND LIGGETT.[77]

In 1917–18 T. H. Liggett and the writer diffused HCl gas in an apparatus similar to that used later by Harkins and Broeker. The separation was interrupted and the atomic weight determinations delayed by the illness of Mr. Liggett. Later work at Central College, in Pella, Iowa, gave chlorine of an atomic weight 35.505 with an increase of 0.045 in the atomic weight over that of ordinary chloride.

The atomic weight determinations were made by the standard method of determining the weight of silver chloride precipitated from a known weight of silver, dissolved as silver nitrate. In each case the determination with ordinary chlorine and the one with the isotopic chlorine were made side by side by the same methods. The chlorine was added in the form of extremely pure potassium chloride, and after long standing the silver chloride was

[77] A more complete account of this work, and especially of the precautions used in the atomic weight determinations, will be published later in the *Journal of the American Chemical Society*.

filtered off on a Monroe crucible (a platinum crucible in which the filtering medium is a thick platinum sponge). The silver chloride was washed while ice cold with ice cold water containing 5 c.c. of 6 *N* nitric acid per litre, and the very small (about 0.00008 g.) correction made for the silver chloride thus dissolved. A perforated platinum disc was kept over the platinum sponge. The crucible with the precipitate was heated at 250° in an electric oven for 10 hours, cooled three hours in a dessicator placed beside the balance, and then weighed. It was heated again, this time for two hours, and cooled and weighed as before. The major portion (90 to 98 per cent.) of the precipitate was then removed from the top of the platinum disc by means of a small metal spatula, and put in a quartz crucible. After weighing, the crucible with the precipitate was heated to 250°, cooled and weighed, and if the loss of weight was greater than 0.00002 gram, it was heated again until the weight became constant. The quartz crucible was then set inside a nickel crucible and heated until the silver chloride fused into one mass. The crucible was rotated to prevent the inclusion of gas bubbles, cooled in a dessicator and weighed. It was then fused again to make sure the weight had become constant. The fusion correction determined in this way was usually about 0.00006 g. per gram of silver chloride.

Weighing.—The balance was a high sensitivity analytical balance made by Ainsworth, and it was found that by taking the null point both before and after the weighings, the samples of silver, for example, could be weighed with not more than 1/100 mg. difference between the weighings. The weights were constantly compared with Class M weights standardized by the U. S. Bureau of Standards.

Purification of the Chlorine.—The solution of hydrogen chloride in pure water, obtained from the diffusions, was distilled in an apparatus of hard glass, and the middle fraction used for further purification. No bromine or iodine could be detected by very careful tests. However, to insure their absence the hydrochloric acid was distilled after a few crystals of potassium permanganate had been added to it, and the middle fraction was used for further purification. The acid was converted to potassium chloride by adding potassium carbonate which had been prepared from quite pure material by several careful recrystallizations in which the amount of the carbonate was reduced to 1/50

its original weight. The potassium chloride thus formed was recrystallized a number of times from very pure water. Both the isotopic and the ordinary chlorine were purified in this way.

Tests for Iodine and Bromine.—Numerous tests were made upon both the fractions and the mother liquors in the several stages of the purification process, but at no time could either iodine or bromine be detected in the isotopic material. For iodine both the nitrous acid and the nitrosyl sulfuric acid test were used. The former would easily detect 1/100 milligram of iodine in 0.8 g. of potassium chloride, while the later would detect 1/10 mg. in the same amount of potassium chloride. It was found that under the same conditions, that is, in the presence of potassium chloride, the chlorine water and carbon bisulphide test would detect 1/10 mg. of bromine when properly used. Since bromine was not found in the mother liquors nor in the purified material, its absence, except in entirely negligible amounts, is certain.

Atomic Weight of the Isotopic Chlorine.—The final heavy fraction from the diffusion gave 3.08 grams of potassium chloride, with a cut of 14,700. This cut should give, in a diffusion which is 100 per cent. efficient, a separation of 0.0912 unit of atomic weight. Actually the separation was 0.045 unit of atomic weight, or the efficiency of the process was 50 per cent., which is slightly lower than that attained by Harkins and Broeker and higher than that of Harkins and Hayes. It will be seen later that the lower efficiency in the last investigation mentioned was due to the fact that the pores in the porcelain tubes used were larger than in the two other sets of experiments. Table XXXVIII A gives the values obtained in atomic weight determinations on the different fractions.

TABLE XXXVIII A.

Atomic Weight Determinations on Isotopic Chlorine by the Standard Method of Precipitation of Pure Silver by Means of the Chloride.

Diffusion.	Approximate Cut.	Atomic Weight.	Mean Atomic Weight.	Over Ordinary Chlorine Increase in Atomic Weight Theory.	Expt.
1		35.466			
		35.473	35.470		0.010
2		35.483			
		35.491	35.487		0.027
3	14,700	35.502			
		35.508	35.505	0.0912	0.045

58. APPARATUS FOR THE SEPARATION OF CHLORINE INTO ISOTOPES BY DIFFUSION THROUGH A POROUS WALL AT ATMOSPHERIC PRESSURE, AS USED BY HARKINS AND HAYES.

Of the methods for the diffusion of a gas through a porous wall, there is little doubt that the most efficient is what is termed a vacuum diffusion, in which the gas diffuses through the wall into as high a vacuum as can be maintained. The pressure on the high pressure or "heavy fraction" side of the wall is kept at a magnitude which is dependent upon the diameter of the pores in the wall, and at such a value (for example, 10 mm. of mercury) that the mean free path of the gas is as great as the diameter of the pores, which should be of uniform diameter. The low pressure of the gas insures not only a molecular passage of the gas through the pores, but it also aids greatly in securing a good mixing of the gas.

There are, however, several objections to the diffusion at low pressures: (1) it is difficult to make the process automatic; (2) the volume of the gas per unit mass is greatly increased, and (3) it necessitates a more cumbersome method of collecting the heavy and light fractions. For these reasons it was decided, since a fair efficiency had been obtained in a separation of known gases, and particularly since a very good (about 60 per cent.) efficiency had been obtained in the separation of the isotopes of chlorine by Mr. Broeker by diffusing at atmospheric pressure, to delay the use of the vacuum method [78] until after the difference in atomic weight of the chlorine separated by this method had been definitely established by the use of this partly automatic apparatus.

The general procedure adopted is to generate hydrogen chloride at atmospheric pressure by dropping concentrated sulfuric acid into concentrated hydrochloric acid from a height of about 90 cm. in order to secure good mixing of the acids. For later diffusions the sulfuric acid is dropped upon sodium chloride. The dried gas is passed through porous porcelain tubes, and the lighter fraction which consists of the diffusate which passes through the walls is swept away by a rapid current of purified air. The heavy fraction is that which passes through the

[78] Two low pressure diffusion apparatuses, for the separation of HCl into isotopes, have been constructed in this laboratory, one by Mr. Mann, and the other by Mr. Harris. One of these is now in use.

system of tubes and remains inside. Both fractions are absorbed by condensation in the *surface* of a considerable amount of water. The apparatus, though quite similar to that used in this laboratory by Doctor Turner and by Mr. Broeker, but not described by them, is greatly improved in many particulars. It was designed to care for 1000 litres of hydrogen chloride per day, at atmospheric pressure.

Only acids of high purity were used in the work, and the hydrogen chloride produced came in contact only with pure sulfuric acid, glass, porous porcelain, and a very small area of paraffin, from the time it left the generators until it was absorbed in distilled water of "conductivity" grade.

Since according to the Rayleigh theory the enrichment of the heavy fraction with respect to the heavy constituent depends only upon the fraction of the original gas that remains inside the diffusion tubes, and since this fraction changes very rapidly with the rate at which the gas is fed into them from the generator, a flowmeter was placed in the line leading from the generator, and the evolution of gas was so regulated that the flowmeter gave a constant reading.

Flowmeters were also placed in all of the air sweep-out lines for each diffusion tube jacket, since it was necessary to reduce the partial pressure of the hydrogen chloride in the diffusate to a very low value as soon as it escaped from the walls of the diffusion tubes, and since otherwise a back diffusion would greatly lower the efficiency of the process.

A 20-litre bottle (1), with a tall dropping head, serves as a generator for the first diffusion. Six litres of C. P. hydrochloric acid is introduced into this bottle through the dropping funnel (2). For each 6 litres of this acid about 8 litres of concentrated C. P. sulfuric acid is dropped into it from a very wide 24-litre supply bottle (3). The flow of acid, after it is started, is controlled by the 3-way stopcock (4), the supply being sufficient to run for 23 hours. By refilling the generator at about 4.00 P.M. each day, a very steady flow of gas is secured through the night, the regulation requiring no attention between 10.00 P.M. and 7.30 A.M. When the speed of generation begins to fall in the morning, the generator is heated to 50° by means of an air-bath heated on an electric hot plate. By this means 75 per cent. of the hydrochloric acid in the original acid can be recovered. The generator is emptied by means of pressure through the siphon (4) directly into a carboy. For all succeeding diffusions the gas is generated in a 2-litre or a still smaller flask (5) into which sulfuric acid is dropped from a funnel (6). When the speed of evolution of gas from this generator falls, it is heated to 100°, thus giving nearly 100 per cent. recovery of the hydrogen chloride.

The trap (7) is to prevent an explosion of the generator, which otherwise is likely to occur if the generator happens to foam over, since the warm sulfuric acid solution of sodium hydrogen sulfate will solidify very quickly when it reaches the cold tubes. This usually clogs the tubes, and an explosion is apt to result, but has never occurred when the trap is in the system.

From the generators the hydrogen chloride passes into the trap (8) which collects moisture and sulfuric acid spray and through the flowmeter (9). Sulfuric acid is used as the manometer liquid in all of the flowmeters, and its injection into the apparatus is prevented by the traps (10). The bulb (11) is used to prevent sulfuric acid from being drawn back into the flowmeter (10) from the gas dryer (12). The thistle tube and its connections on (12) served to introduce fresh acid into the dryer, and also as a manometer to measure the pressure at the generator end of the diffusion train. The drying acid in (12) is renewed every second day. The bulb (13) is filled with glass wool, tightly packed, to filter out all sulfuric acid spray from the dried gas. After passing this the gas goes directly into the first diffusion tube (14). The first diffusion tubes are the stems of churchwarden pipes, while the succeeding ones were especially prepared for our use by the Ceramics Division of the Bureau of Standards. The latter are one metre long, 11 mm. outside diameter, with 2 mm. walls. They are sealed into glass tubes of almost the same diameter by the use of plaster-of-Paris. The diffusion tubes are then sealed into glass jackets 1.5 metres long, and 5 cm. in diameter. The air for sweeping out the diffusate enters the jackets through the two tubes (15) and passes out of it through the three tubes (16). These three exit tubes for each jacket are assembled into a single line leading to the absorbers for the light fraction. During the first diffusion the material from the first diffusion unit is absorbed in distilled water in absorber (17) and is designated as the light fraction from the first diffusion. During later diffusions of the heavy fraction this absorber is shunted out of the line, since its capacity is too great. The diffusate from the succeeding 4 jackets is absorbed in the large absorber (18) and when the concentration of the solution reaches 6 *N*, it is turned back into the stock of the laboratory (not, however, for any diffusion after the first) as diluted chemically pure hydrochloric acid. It is free from sulfites, sulfates, organic matter, and gives no test for iodine or bromine. The heavy fraction, or that which remains inside of the tubes at the end of the fifth or last unit, is absorbed in the absorber (19).

In the third and fourth diffusions only the first two units are used, and the small absorber (20) is used for the heavy fraction. Very large 3-way stopcocks (22) are between each two diffusion units, so that the apparatus may be used as two or more separate diffusion trains. The series of bulbs and the dropping funnel (21) constitute a sulfuric acid dryer for the heavy fraction passing from the fifth unit to the absorber (19), its purpose being to prevent any moisture from the absorber from reaching the porous tubes. The absorbers were all made on the same plan, and consist of two or more horizontal, and usually very large, glass tubes, arranged one above the other. Each of these tubes is provided with a gas inlet tube at one end, and an outlet tube at the other, and also with a tube and stopcock for allowing the acid to

be dropped into the next unit below, or, on the bottom or first unit, for drawing it off from the apparatus.

The horizontal tubes are filled nearly full of pure distilled water, thus leaving a long narrow passage for the gas. Nearly all of the hydrogen chloride is absorbed in the first unit, and none of this gas can be detected by the odor at the exit from the last tube. When the solution in the first or bottom tube reaches 6 *N* in concentration, it is drawn off, the solution in each of the other tubes is dropped into the tube just below it, and distilled water is poured into the last or uppermost tube. This change can be made during the operation of the apparatus, while the method of surface absorption makes it possible to keep the pressure in the tubes very close to that of the external atmosphere, and to balance properly the pressures inside and outside the tubes, so that capillary transpiration may not occur.

The air supply for sweeping out the diffusate from the jackets comes from the compressed air supply of the laboratory, and is passed into an empty bottle (23) for settling out impurities, then through 30 per cent. caustic soda solution in the very large bottle (24), through the safety bottle (25), through concentrated sulfuric acid in a very large bottle (26), and is then blown on the surface of concentrated sulfuric acid in the bottle (27). It is then filtered through a foot of glass wool (28) and a foot of absorbent cotton (29), and passes into the distribution line (30). From this it flows through individual stopcocks (31), through flowmeters (32), past sulfuric acid manometers (33), through traps (34) into the jackets of each unit. The traps are used to prevent sulfuric acid from getting into the diffusion units from the manometers or flowmeters. The manometer (35) and that at (12) serve to give the gas pressure in the diffusion line, while those designated as (33) indicate that in the jackets.

Air is passed through each jacket at the rate of 3 litres per minute. During first diffusion hydrogen chloride passes flowmeter (9) at the rate of 600 c.c. per minute, and at this rate one-thirtieth of it arrives at the absorber for the heavy fraction (19) and is collected there. For the second diffusion, gas is generated at the same rate, but only four of the units are used. This gives a cut of 20. Third diffusions are run with only the first two units, gas being generated at the rate of 200 c.c. per minute, and again a cut of 20 results. The total cut $30 \times 20 \times 20$, or 12,000, should, according to the Rayleigh theory, give an atomic weight for the chlorine in the heavy fraction of 35.54, but it is hardly to be expected that an efficiency of 100 per cent. in terms of this theory can be obtained, except possibly in a vacuum diffusion under ideal conditions.

The heavy fraction from each diffusion is neutralized with very pure sodium hydrogen carbonate, and is used in the generator which uses salt (5) for the regeneration of the hydrogen chloride. It is found that the generation from sodium chloride occurs at a more uniform rate if carried out at a temperature of 80° until the charge is nearly spent, when the temperature is rapidly raised to 100°. If the generator at the middle of the run is giving off gas at the rate of over 300 c.c. per minute, the salt cake will adhere to the bottom of the flask, until enough sulfuric acid has been run in to float it. Just as it comes loose from the bottom of the flask there is a violent evolution of gas.

At rates below 300 c.c. per minute the cake is gradually wetted throughout with sulfuric acid and the difficulty is avoided.

It is evident that the process of diffusion may be carried out fractionally and this was done. Thus the light fraction from the second diffusion has nearly as high a density as the heavy fraction from the first diffusion, so it is not rejected, but is rediffused, and the heavy fraction which results has nearly as high a density as that of the original second diffusion.

59. METHOD OF ANALYSIS AND CALCULATION OF RESULTS.

In order to be able to determine the effects of the successive diffusions it is important to develop a method of determining with considerable precision the change of atomic weight produced. It was found that such a method could be devised easily, provided a simple and seemingly accurate hypothesis is adopted as its basis. This is that isotopes have so nearly the same atomic volumes and the same chemical properties, that no error of sufficient magnitude to affect the analyses will be introduced if it is assumed that they are exactly alike in these respects. That the isotopes of lead have the same volume within the limits of the experimental error has been shown by Soddy [79] and by Richards [80] and that their identity in chemical properties is almost complete is demonstrated by the work on the spectra of the isotopes of lead described in section 53 of the present paper, which shows the identity in this respect to one part in a million.

However, even though this hypothesis is used as a basis for calculation, the proof that a *separation* of the two isotopes of chlorine has been made is *entirely independent* of the assumption, since no differences of atomic volume could be detected unless a separation had first been effected.

The simplest method for determining the increase of atomic weight was thought to be the determination of the densities of specimens of highly purified ordinary hydrochloric acid, and a comparison with these of the density of a specimen of acid produced by diffusion, which will be termed the isotopic acid. The plan adopted was to fix the molecular concentrations of these two acids as determined by titration, at the same value, and to

[79] Soddy: *Nature*, **94**, 615 (1915).

[80] Richards: *J. Am. Chem. Soc.*, **38**, 221 (1916); and "Presidential Address to the American Association for the Advancement of Science," 1918.

compare the weights of hydrogen chloride which they contain. It is evident that the weight of the isotopic acid should be greater than that of the ordinary or "comparison" acid, since the present discussion refers to the heavy fraction. These weights are in the same ratio as the formula weights of hydrogen chloride in the two solutions, so

$$M_i = 36.468 \cdot W_i/W_c \quad (1)$$

and

$$A_i = M_i - 1.008 \quad (2)$$

or

$$\triangle A = 36.468\,\triangle W/W_c. \quad (3)$$

Here M_i and A_i are the molecular weight of hydrogen chloride and the atomic weight of chlorine, respectively; W_i and W_c are the weights in grams of the hydrogen chloride in the same volumes (*e.g.*, pycnometer full) of the comparison and the isotopic acids, and ΔW is the increase in weight which occurs when the isotopic acid is substituted for the comparison acid. Equation 3 gives the most accurate results, since it does not involve an exact knowledge of the weight in solution of either the comparison or the isotopic acid, but only a precise value for the increase in weight. The thermostat should be regulated to 0.001° or better, and the pycnometer should consist of a large spherical bulb with a short but very narrow neck graduated with a very fine line at its narrowest point. Above the neck is a bulb large enough to hold any solution which rises through the neck on account of thermal expansion. This is fitted with a very close fitting ground-glass stopper, and with very fine tubes for filling and emptying.

While the above procedure is the simpler from the standpoint of the equations involved, it happens that another method is more economical of time and material, so what has actually been done in most of the cases is to adjust the comparison and the isotopic acids to the same density, and to determine the number of molecules of hydrogen chloride, and therefore the number of atoms of chlorine, present by titration. In this case the acid in the pycnometer has a higher molecular concentration when the comparison acid is used. Very accurate density determinations have been made on solutions of very pure ordinary hydrochloric acid by Dull in this laboratory. From his data it may be calculated that the "apparent density" of hydrogen chloride in 5.91 N hydrogen chloride is 1.785, in 5.79 N it is 1.7852, while in 5.20 N it is 1.787, and in 2.315 N it is 1.856.

The difference in the titration values of the comparison and the isotopic acids may easily be calculated in the following way for any desired increase in the atomic weight ($-\Delta A$) of chlorine. Calculate the increase of weight which would occur if the comparison acid in the pycnometer were to be replaced by isotopic acid of the same titration value. Then calculate the number of equivalents of hydrogen chloride in the isotopic acid which must be replaced by water of a density 0.997077 (or 0.99604 as weighed by brass weights in air, if the temperature of the thermostat is 25°) in order to reduce its weight by the above difference. This gives the difference in the titration values of the two solutions when adjusted to the same density, which will be given directly in terms of 0.01 N sodium hydroxide solution, since the titration was completed with a base of this concentration, though begun with 1 N solution.

$$\Delta T = \frac{V.\ N\Delta A}{1000.\ M_c} \cdot \frac{\mathrm{dHCl}}{\mathrm{dHCl}-\mathrm{dH_2O}} \cdot \frac{1}{10^{-5}} \qquad (4)$$

or

$$\Delta A = \frac{100.\Delta T}{} \cdot \frac{\mathrm{dHCl}-\mathrm{dH_2O}}{\mathrm{dHCl}} \cdot \frac{M_c}{V.N}. \qquad (5)$$

Here the symbols have the same meaning as before, except that the following new ones are employed: M_c is the equivalent weight of hydrogen chloride in the comparison acid, and equals 36.468 in the present experiments; N is the normality of the comparison acid; dHCl is the apparent density of hydrogen chloride in the comparison acid; $\mathrm{dH_2O}$ is the density of water at the same temperature; ΔT is the difference in grams of $^1/_{100}$ weight normal sodium hydroxide between the pycnometer full of the two acids; 10^{-5} is the number of equivalents of sodium hydroxide in 1 c.c. of 0.01 N base. V is the volume of pycnometer in c.c. If V c.c. is titrated, the right-hand side of the Equation (5) for ΔA should evidently be multiplied by V/v.

Let T'_c and T'_i represent the titration values of the comparison and isotopic solutions in terms of normal solutions, then it is evident that Equation 5 may be given the following form:

$$\Delta A = \left(\frac{T_c}{T_i} - 1\right) \frac{\mathrm{dHCl}-\mathrm{dH_2O}}{\mathrm{dHCl}} \cdot M_c \qquad (6)$$

Method of Adjusting the Densities of the Isotopic and Comparison Acids.—After a preliminary determination of the densities of the two solutions, the concentration of the solution was read from a graph giving concentrations in terms of the density

of ordinary pure hydrogen chloride, and from these values the amount of water necessary to decrease the concentration of the more concentrated solution to that of the more dilute was calculated. This first adjustment brought the densities of the solutions sufficiently close so that a difference of 5 or 6 mg. was all that remained for a volume equal to that of the pycnometer.

A second dilution was made by adding water up to the exact amount called for by the equation $(d_1d_2 - d_2).W_w = W_s(d_2d_1)$, where d_1 is the smaller, and d_2 the larger density, W_w is the weight of water to be added to the weight W_s of the more dense solution in order to make the densities the same. This equation is not exact, since it takes no account of the volume change produced in adding water to approximately 6 *N* acid, so it does not bring the two weights closer together than 0.6 mg. An exact equation could easily be developed, but even with the form used only 0.2 g. of water had to be added to 75 g. of solution in the third dilution.

Error of Filling.—The pycnometer could be filled repeatedly with a *maximum* variation of 0.0012 per cent., while the usual error was considerably less. The thermostat was constant to within less than 0.001°.

Method of Titration.—First a series of indicator standards was made up in 125 c.c. tightly glass-stoppered Erlenmeyer flasks.[81] In each of these was put the same volume of conductivity water and the same amount of methyl orange as was used in the titrations. To these were added in order 0, 2, 4, and 6 drops of 0.01 *N* hydrochloric acid. The titrations were ended at a color between that in the two-drop and the four-drop flasks, and in good daylight the effect of one drop of 0.01 *N* base could be readily detected. A 1 *N* solution of sodium hydroxide was used to carry the titration to within one drop of the end-point, when it was finished with 0.01 *N* solution of the same base. Weight burets of 60 g. capacity were used and these were weighed on a balance sensitive to 0.02 mg. It was found that the use of a heavy " vacuum " stopcock grease completely stopped all loss of weight of the burets due to evaporation of the solutions through the ground-glass stopcocks.

[81] Flasks with very narrow necks will be used for all future work, so that the evaporation may be decreased.

The samples for titration were weighed by measuring 5 c.c. of the 6 *N* solution, dropping it into the flask, and then determining the weight on the same balance as that used for the pycnometer. The ground-glass stoppers in the sample flasks were kept dry during the whole determination.

60. PURIFICATION OF ACID.

The acid used in the analyses as the reference or comparison acid was the light fraction from the first diffusion. A calculation showed that its atomic weight could not have been changed sufficiently to be detectable, and the process used would result in a considerable purification. The acid was treated with potassium permanganate and boiled to expel any iodine, bromine, or chlorine liberated, and was then distilled, rejecting the first third and the last one-fourth.

The isotopic acid was purified in several ways. As has been stated it was formed by the action of very pure sulfuric upon C. P. hydrochloric acid. The gas came in contact with only carefully cleaned and dried glass and porous porcelain, and was absorbed in conductivity water. After the second diffusion the salt formed by neutralizing the acid by very pure sodium hydrogen carbonate was recrystallized three times from pure water and was very thoroughly drained and washed with pure water each time. The mother liquor from these crystallizations showed no trace of iodine by the use of a test which would detect one part of iodine as iodide in twenty thousand parts of sodium chloride, as determined by repeated tests. This test consisted in the use of nitrosyl sulfuric acid and carbon disulfide with the proper precautions. Neither could bromine be detected in these mother liquors, but we did not rely upon this fact to insure the absence of bromine. In addition to these three crystallizations, the acid, after the third diffusion, was treated with potassium permanganate and distilled, using exactly the method employed with the comparison acid, except that the first and last fourths were rejected and the middle half was saved. Additional purifications were made by precipitation of sodium chloride from aqueous solution by the addition of isotopic hydrogen chloride. The sodium hydroxide used in the analyses gave no test for bromine. It was converted into sodium chloride and recrystallized, and the mother liquor again gave no test for bromine.

However, after the sodium hydroxide was added to any sample the latter was always purified carefully. Still further careful purifications were employed, as described in another paper,[82] but what is given above will be sufficient for inclusion here.

61. ANALYSIS OF THE PURIFIED THIRD DIFFUSION RESIDUE (Cut = 12,000).

In order that the magnitude of the errors involved may be realized the actual data for some of the analyses will be presented. First the reference acid and the isotopic acid were adjusted to practically the same density in a Harkins' pycnometer of about 22 c.c. volume. The weights were as follows:

TABLE XXXVIII B.

Analyses.

	First Series.		Second Series (after another distillation).	
	Weight *in vacuo* of pycnometer plus.			
	Reference acid.	Isotopic acid. ($t \pm 25° \pm 0.0005°$)	Reference acid.	Isotopic acid.
1.	37.2533	37.2530	37.2100	37.2095
2.	37.2535	37.2527	37.2100	37.2098
Av.	37.2534	37.25285	37.2100	37.20965
Diff.	0.00055 g. = 0.00148%		0.00045 g. = 0.00121%	

TABLE XXXVIII C.

Data on the Atomic Weight Determinations.

(Note that the two columns on the left of the table refer to one set of analyses, the two on the right to a second series.)

No. of mols. of HCl in 100 g. of sol.; from density.	First Series. $N = 5.91$	Second Series. $N = 5.79$
Density of Isotopic Acid.	1.10195	1.00983
Bar. Pressure = 748.4 mm. ($h = 7.17$)* to 746.5 mm. ($h = 10.4$).		$t = 24°$ to 26°.
Wt. of pycnometer of water.		35.0350
Wt. of pycnometer.		13.2765

* The absolute humidity in mm. of mercury is represented by h.

[82] Harkins and Hayes: *J. Am. Chem. Soc.*, **43**, page 1822 (1921).

Data for the Titration of the Reference and Isotopic Acids.†

First Series.	NaOH used per 5 g. of acid.		Second Series.
26.2613	26.1970	25.7887	25.7173
26.2669	26.2004	25.7848	25.7188
			25.7120
Av. 26.2641	26.1987	25.7867	25.7160
Diff. (g. of 0.01 *N* NaOH) 6.54			7.07
	After standing for one day.		
26.2630	26.2030	25.7755	25.7094
26.2673	26.2069	25.7745	25.7064
	26.2030	25.7752	
Av. 26.2651	26.2043	25.7751	25.7079
Diff. (g. of 0.01 *N* NaOH) 6.08			6.72
	After standing for two days.		
		25.7695	25.7045
		25.7671	25.7002
	Av.	25.7688	25.7023
Diff. (g. of 0.01 *N* NaOH)			6.65

Increase of Atomic Weight.

	First Series.			Second Series.		
	Uncorr.	Correction for density.	At. wt. increase.	Uncorr.	Correction for density.	At. wt. increase.
1st set.	0.0356	−0.0018	0.0338	0.0393	0.0016	0.0377
2nd set.	0.0331	−0.0017	0.0312	0.0374	0.0015	0.0359
3rd set.				0.0370	0.0016	0.0354
Av. increase in at. wt.			0.0325			0.0363
Average of Series 1 and 2			0.0344			

100 g. of chlorine obtained of atomic weight 35.494.

† The weights of base and acid used in these titrations are reduced to the same barometric pressure and the same humidity for each series.

The corrections of about 0.0018 for the results of the first, and of 0.0016 for the results of the second series were calculated from the density differences by means of the same equation as was used for the calculation of the results of the titrations.

The difference between the averages of the atomic weights for the first and second series of analyses is 0.0038 unit of atomic weight which is very near the possible error in the atomic weight of chlorine according to Richards. While the data given indicate that the comparison method described is a very accurate

one for the determination of the atomic weight of an isotope of chlorine, our experience has shown that its precision may be increased, provided as large quantities of acid are available, by the observance of certain precautions which may be introduced. The atomic weight of the chlorine produced by diffusion by the writers is very close to 35.494, while that obtained by Harkins and Broeker was 35.515. However, the amount of material produced by the present work is very much greater.

62. REPURIFIED FOURTH DIFFUSION RESIDUE (Cut = 240,000).

The hydrochloric acid obtained from the third diffusion had been converted largely into sodium chloride in the titrations on the third diffusion residue, so the remaining acid was neutralized with sodium hydrogen carbonate. The salt thus obtained was converted into hydrogen chloride, and again diffused. The hydrochloric acid thus obtained was distilled fractionally, after heating with potassium permanganate. The middle portion was used for the analyses reported below.

TABLE XXXIX.

Analyses.

	Reference acid.	Weight *in vacuo* of pycnometer plus (l, 25° + 0.0005).	Isotopic acid.
1.	36.4461		36.4465
2.	36.4460		36.4465
Av.	36.44605	Diff. 0.00045	36.4465

No. mols. in 1000 g. solution from density. Density of isotopic acid.

$N = 5.22$ $d^{25} = 1.08868$

Barometric pressure = 737 to 739 mm. Absolute humidity = 7.6 to 7.05 mm.

Temperature = 24 to 26°.

Data for the Titration of the Reference and Isotopic Acids.

(All weights corrected to 737 mm. and $h = 7.6$.)

N NaOH per 5 g. of acid.

Reference acid.	Isotopic acid.
First Day.	
G.	G.
23.3430	23.2898
23.3456	23.2870
23.3443	23.2884

Diff. 5.59 g. of 0.01 N NaOH.

Second Day.

23.3359	23.2793
23.3401	23.2785
23.3369	23.2755
23.3376	23.2778

Diff. 5.98 g. of 0.01 *N* NaOH.

Increase in Atomic Weight above 35.46.

	Uncorr.	Correction for density.	Atomic weight increase.
1st day's determinations	0.0346	Add. 0.0017	0.0363
2nd day's determinations	0.0370	0.0017	0.0387
		Av.	0.0375

Nine g. of chlorine as hydrogen chloride of atomic weight 35.498 were obtained in this diffusion. The fourth diffusion was not so efficient as the first three, since the apparatus is better designed for larger samples, and in this diffusion the gas passed through only a short length of porous tube of large diameter.

63. APPLICATION OF THE ELEMENTARY THEORY OF DIFFUSION TO THE SEPARATION OF ISOTOPES BY DIFFUSION OR BY AN IRREVERSIBLE EVAPORATION.

One of the most simply derived of all of the relations of the kinetic theory of gases is that which states that the mean velocity of the molecules of a gas varies inversely as the square root of the molecular weight. Upon the basis of this relation Lord Rayleigh [83] in 1896 developed an equation which makes it possible to calculate the enrichment of a diffusion residue with respect to the heavier molecules in a mixture of *two gases*, as the cut increases. The cut may be defined as the number of mols of the initial mixture which have given 1 mol of the heavy fraction in question. Table XL illustrates the change of atomic weight of neon and of chlorine with the cut.

This table indicates that it is easier to secure a change of 0.1 unit in the atomic weight of chlorine than in that of neon, if the cut alone is taken into account. The conditions are also more favorable to the chlorine from the point of view of abundance, ease of handling, and ease of purification. It will be seen that to secure 10 grams of chlorine with this increase of atomic weight, it would be necessary to start with 186 kilos of chlorine in the form of hydrogen chloride, provided the intermediate frac-

[83] *Phil. Mag.* (5), **42**, 493 (1896).

tions are not refractionated. This involves the assumption that the efficiency of the process is kept equal to 100 per cent., which is by no means easy.

TABLE XL.

Values of the Cut $(X+Y)/(x+y)$ Necessary for Increase of the Atomic Weights of Chlorine and of Neon by Definite Amounts. A Diffusion of the Heavy Fraction. (Chlorine diffused as hydrogen chloride.)

(Percentage of isotope of atomic weight 37 in chlorine = 23, of atomic weight 22 in neon = 10.)

Increase of atomic weight.	Chlorine. Cut.	Chlorine. Corresponding enrichment.	Neon. Cut.	Neon. Corresponding enrichment.
0.05	160	1.1459	217	1.286
0.10	18,600	1.302	19,600	1.588
0.15	1,690,000	1.469	991,000	1.909
0.20	117,000,000	1.648	33,000,000	2.25

Mulliken and Harkins,[84] in a paper from which much of the following material has been taken, have developed equations which bring to light the various factors involved in the separation. Their more complete equations give the enrichment of the light, as well as the heavy fraction, and also apply to a mixture of any number of isotopes. On account of the more general applicability of their equations the discussion given in the present paper will be based on their system of treatment.

Almost the only discussion, other than our own, of the application of the theory of gaseous diffusion to the separation of isotopes, has been given by Lindemann and Aston,[85] and by Aston,[86] on the basis of the *equation of Rayleigh*. In these discussions too much weight has been placed on the diffusion exponent, and too little on the composition of the isotopic mixture which constitutes what we know as the element. Thus Aston (*loc. cit.*) states that the most favorable case known for the separation of isotopes is that of neon, since only the 21st root is involved as the diffusion exponent.

What is the most favorable case depends not only upon the facts, but upon the point of view. Thus the aim of the work may be to attain:

1. The greatest possible difference of relative density.
2. The greatest possible difference of atomic weight.
3. The most complete separation of the isotopes.

[84] *J. Am. Chem. Soc.*, **44**, 37–65 (1922).
[85] *Phil. Mag.*, **37**, 53 (1919).
[86] "Isotopes," p. 130.

It is obvious that these are not the only factors, since the amount of material obtained (number of mols) is also of prime interest.

It is easy to show that for a mixture of two isotopes the *rate of separation* is as follows:

A. *In Terms of Relative Density.*	B. *In Terms of Change of Atomic Weight.*
1. Proportional to the square of the interval between the molecular weights.	
2. Proportional to the product of the mol-fractions of the isotopes.	
3. Proportional to the logarithm of the cut.	
4A. Inversely proportional to the *square* of the ordinary molecular weight.	4B. Inversely proportional to the ordinary molecular weight.

It will be seen that *only the fourth factor is different in the two cases. For a given element the rate of separation in either sense is inversely proportional to the molecular weight of the compound in which the element is combined.* The second factor listed above indicates *that the most favorable mixture for the separation of two given isotopes is that which consists of fifty (molar) per cent. of each.*

The increase in molecular weight (ΔM) is given approximately by the following simple equation:

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{M_2} \ln C = B \ln C$$

in which M_1 and M_2 are the molecular weights of the light and heavy isotopes, respectively, x_1 and x_2 are the corresponding mol fractions, and C is the cut. B, which is aproximately constant, is the *separation coefficient,* with respect to the molecular weight. *The rates of separation of the isotopes of various elements are proportional to the corresponding values of B.*

64. THE RATE OF SEPARATION OF VARIOUS NATURAL ISOTOPIC MIXTURES.

The relative rates of separation of all of the elements whose isotopic composition is known quantitatively are shown by Table XLI, in the form of the separation coefficient B, which gives also the absolute rate of separation. *This table is of great value, since it is the first to give this important information.*

If, for example, neon and hydrogen chloride are compared, it is found that the latter has the higher separation coefficient. If the approximate equation given above is considered, it is seen that $(M_2 - M_1)^2$ is the same for both of these elements, while the molecular weights give a factor of $\frac{36.46}{20.20}$ or 1.805 in favor of the

neon. However, the product of the mol fractions is 0.0900 for neon and 0.1771 for hydrogen chloride, thus giving a factor equal to 1.970 in favor of hydrogen chloride. Though the initial diffusion coefficient is thus more favorable in the case of hydrogen chloride, if an extensive series of diffusions is carried out, it is

TABLE XLI.

Composition and Separation Coefficients of Isotopic Mixtures.

Element of compound.	At. wt. or mol. wt.	At. or mol. wts. of isotopes.	Corresponding mol-percentages.	$1-k\sqrt{2}$	B or B'/n_E	E or E'/n_E
Li	6.94	6,7	6.94	0.0742	0.00450	0.00403
B	10.9	10,11	10.90	0.0466	0.00438	0.00409
BH_3	13.9	13.14	10.90	0.0364	0.00339	0.00322
Ne	20.2	20,22	90.10	0.0466	0.00843	0.00818
Mg	24.32	24,25,26	79.10,11(?)	.....	0.00868	0.00843
HCl	36.46	36,38	77.23	0.02668	0.00950	0.00932
CH_3Cl	50.46	50.52	77.23	0.01941	0.00690	0.00681
Cl_2	70.92	70,72,74	59 .3,35 .4,5 .3	.....	0.00494	0.00499
CH_2Cl_2	84.92	84,86,88	59 .3,35 .4,5 .3	.....	0.00413	0.00417
$CHCl_3$	119.38	118,120,122,124	4.7,40 .9,12 .2,1 .2	.....	0.00295	0.00296
CCl_4	153.84	152,154,156,158, 160	35 .2,42 .0,18 .8,3 .7,0 .3	.....	0.00229	0.00231
Ni	58.68	58,60	66,34	0.01680	0.00758	0.00747
$Ni(CO)_4$	170.68	170,172	66,34	0.00582	0.00262	0.00260
Zn	65.37	64,66,68,70	51 .5,31,15,2 .5(?)	.....	.....	0.02037*
K	39.10	39.41	95.5	.....	.....	0.00232
Rb	85.45	85,87	77 .5,22 .5	.....	.....	0.00409
Kr	82.92	78,80,82,83,84,86	0.15,18,16,25,30	.....	.....	0.0306
HBr	80.92	80.82	54,46	0.01228	0.00614	0.00606
Hg	200.6	197–200,202,204	.....	.....	0.0063	(experimental)†

* These values of E are practically the same as the values of B in the cases of Zn, Rb, and Kr. E is the separation coefficient calculated from a less exact equation than that used in the calculation of B. The meaning of the column $1-k\sqrt{2}$ may be found in the later sections of the paper in which the equations involving B and E are developed.

† The value 0.0063 for the separation coefficient of mercury was determined by *diffusion* at low pressures through a membrane of filter paper. The highest separation obtained by the method of vaporization at low pressure corresponds to a value for the coefficient of 0.0057.

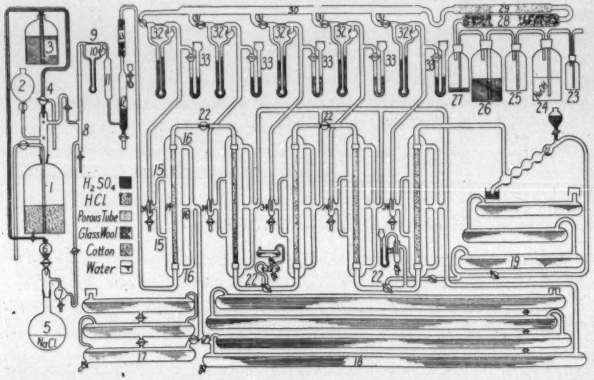
found that in the case of the *heavy fraction* the diffusion coefficient for both substances increases as the diffusion proceeds, but much more rapidly for neon, so the diffusion coefficient of the latter soon becomes the larger. However, with the *light fraction* the diffusion coefficients of both become less favorable, and that of neon becomes less favorable even more rapidly than that of hydrogen chloride.

The compounds of chlorine listed in the table indicate that if Cl, Cl_2, Cl_3, and Cl_4 could be diffused, the relative rates of separation in terms of the change of atomic weight (separation coefficient) would be, respectively, 1, $1/2$, $1/3$, and $1/4$. The values given in the table are slightly different from what would be expected from these ratios, since all but Cl_2 are loaded with either hydrogen or carbon.

The highest rate of separation for an *element* of given isotopic composition is that for monatomic molecules of the pure element.

The separation coefficient B/n_e is very nearly inversely proportional to the total molecular weight (see table), whether the molecule contains one or more atoms of the isotopic element. When n_e, that is, the number of atoms of the isotopic element (*i.e.*, 4 in CCl_4), is greater than 1, the presence of different isotopes in a single molecule tends to reduce the separation coefficients, as pointed out in connection with molecular chlorine. This is, however, balanced by the effect of the large difference in molecular weight of the lightest and heaviest molecular isotopes, so that the

FIG. 29.



effect of the total molecular weight, as indicated by Equations 7A and 7A′ given later, is alone effective. For the separation of the element chlorine, hydrogen chloride is evidently the most favorable compound. The separation coefficient of mercury is rather low, but this is more than compensated, from the experimental standpoint, by the chemical inactivity, volatility and ease of purification of the element, and the accuracy with which changes in atomic weight can be determined by density measurements. According to the theory of Harkins,[87] many or most of the *even-numbered elements* above nickel should contain numerous isotopes. In agreement with this, Aston has found 6 or 7 isotopes each for the elements krypton, xenon, and mercury, and 8 for tin. The wide separation of the extreme atomic weights tends to give

[87] *J. Am. Chem. Soc.*, 37, 1367 (1915).

such elements a large separation coefficient, if the extreme components are present in any considerable proportion, for the coefficient depends on the *squares* of the intervals in atomic weight between isotopes (see Equation 7A').

Such elements as selenium, cadmium, tin, and tellurium, should, on this basis, and in the absence of specific information as to the isotopic composition, be favorable cases for separation. Experiments upon zinc and cadmium have been begun in this laboratory.

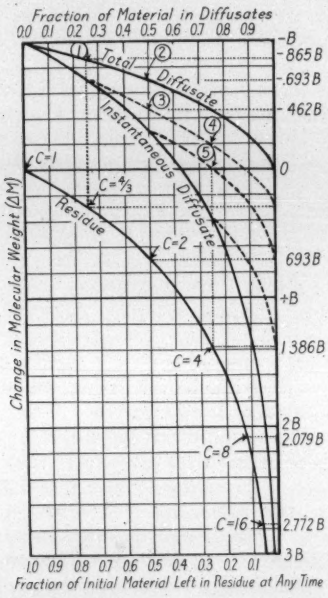
For elements or compounds containing more than two isotopes, it is possible to calculate from the coefficient E a virtual atomic or molecular weight interval $(\Delta M)_v$ corresponding to the case of only two isotopes. For example, the mixture of isotopes in mercury is equivalent to an equimolal mixture of two isotopes having an atomic weight difference of 3.15 units. This is obtained by putting $\frac{(\Delta M)^2 x_1 x_2}{2M} = E = 0.0063$, setting $x_1 = x_2 = 0.50$, and solving for ΔM: $(\Delta M)_v = \sqrt{8EM}$. For magnesium, $(\Delta M)_v = 1.32$; for hydrogen chloride, 1.68; for chlorine, 2.44; for carbon tetrachloride, 3.4; for zinc, 3.3, etc.

The progress of a separation of any number of isotopes can be predicted very closely by the use of Fig. 30, which relates to a process whose efficiency is 100 per cent. This figure indicates that at the beginning of a diffusion process, or of an irreversible evaporation, the diffusate has a molecular weight which is B units less than that of the mixture, and is thus 0.020 unit lighter for zinc, 0.00932 unit lighter for HCl, 0.0063 unit lighter for mercury, etc. The composition of the diffusate leaving when the residue contains about 37 per cent. of the material, is the same as that of the initial material, and the density of the diffused material increases above that of the initial substance as the mass of the residue decreases beyond this value (curve for the "Instantaneous Diffusate"). When the cut has reached 16, that is when 1/16 of the original material is in the residue, the atomic weight of the residue or heavy fraction is 2.77 B units higher, and that of the instantaneous diffusate being collected (light fraction) is 1.77 B units higher than the initial atomic weight.

It is of considerable importance in the experimental separation to keep in mind that the curve for the instantaneous diffusate is such that the molecular weight of the diffusate is always just B units less than that of the residue. However, it should be noted

that B is not actually constant, but that it changes slowly as the separation proceeds. Thus the separation coefficients (B) for neon and hydrogen chloride increase as the separation proceeds, while that for lithium decreases. When more than two isotopes

FIG. 30.



Generalized plot showing atomic or molecular weight of fractions obtained during a 100 per cent. efficient diffusion or irreversible evaporation of a mixture of isotopes.

are involved the variation of the separation coefficient is less simple, but may be easily calculated in each specific instance.

The curves are based on Equations 7, 12, and 16, of the text. The ordinates are expressed in terms of the "separation coefficient" B as a unit; this has a different numerical value (usually about 0.003 to 0.02) for each element (see Table I, and text). The value of B changes slightly with ΔM. The symbol C stands for the "cut" or *ratio* of quantity of material in the *residue* at any time to the *initial* quantity; for any abscissa on the lower scale, the "cut" is merely the reciprocal quantity. The "instantaneous diffusate" curve gives at any point the composition of the material which is at any instant diffusing

or evaporating from residual material corresponding to the same abscissa. Note that this curve has exactly the same form as the residue curve, and differs only in an upward displacement of the ordinates by B units. Each point on the "total diffusate" curve gives the average composition of the material which has diffused or evaporated from the beginning up to that point. The various dotted curves give the composition of *fractions* of the total diffusate beginning at various points *after the beginning of the operation*. The meaning of the total diffusate curves can be made clearer by a few examples. Thus, Point I gives the composition of the diffused or condensed fraction for the interval 0–25 per cent.; Point 2, for the interval 0–50 per cent.; 3, for 25–50 per cent.; 4, for 25–75 per cent.; 5, for 50–75 per cent. Taken in connection with the residue curve, the total diffusate curves show how the original material can be divided efficiently into isotopic fractions. For example, the curves show that the diffusate might be collected in fractions as follows: 0–25 per cent., $\Delta M = -0.865B$; 25–50 per cent., $\Delta M = -0.462B$; 50–75 per cent., $\Delta M = 0$. If the operation were stopped here, the residue would have the atomic or molecular weight $M + 1.386B$, if M is the original atomic or molecular weight.

65. EQUATIONS FOR THE SEPARATION OF ISOTOPES BY DIFFUSION AND EVAPORATION.

It seems of value to collect here the simpler equations, to be developed later in this paper, which refer to the separation of isotopes by diffusion, irreversible evaporation, thermal diffusion, or centrifuging. The numbers of the equations are the same as are used in the later development.

For a mixture of two isotopes, the equations for the residue in an evaporation or diffusion process are

$$\triangle x_2 = \frac{(1-k)x_1x_2}{2(x_1+kx_2)} \cdot \ln C = A \ln C \tag{6}$$

or, approximately, $$\triangle x_2 = \frac{(M_2-M_1)\,x_1x_2}{2M} \cdot \ln C \tag{6A}$$

and $$\triangle M = A(M_2-M_1)\ln C = B \ln C \tag{7}$$

or approximately, $$\triangle M = \frac{(M_2-M_1)^2 x_1x_2}{2M} \cdot \ln C \tag{7A}$$

Similar relations hold for a mixture of any number of isotopes. The x's denote mol-fractions, the M's atomic or molecular weights; $K = \sqrt{M_1/M_2}$; and C, the "cut," is the ratio of the initial to the final number of mols present in the residue.[88] The

[88] In the case of gaseous diffusion, the numerical factor in the denominator is not necessarily 2, but probably is close to 2, in most cases; the same applies to the exponent c in the value of k; *in general* $k = \sqrt[c]{M_1/M_2}$

subscript 1 refers to the lighter, 2 to the heavier isotope. M without a subscript stands for the ordinary, average, atomic or molecular weight. B is called the separation coefficient. For the diffused or evaporated material, the equations are $-\Delta x_2 = A \ln \frac{C}{C-1}$ (15), and $-\Delta M = B \ln \frac{C}{C-1}$ (16). The *total difference* in atomic weight between the two fractions is then

$$\triangle\triangle M = \triangle M - (-\triangle M) = [B + B/(C-1)] \ln C = B.\ C. \ln \frac{C}{C-1} \quad (19)$$

$$= \frac{(M_2 - M_1)^2 x_1 x_2}{2M} \cdot \frac{C}{C-1} \cdot \ln C, \text{ nearly.} \quad (19A)$$

For $C = 1$, $\triangle\triangle M = B$; for $C = 2$, $\triangle\triangle M = 2B \ln 2 = 1.386\, B$;
for $C = 4$, $\triangle\triangle M = (8/3)\, B \ln 2 = 1.848\, B$; etc.

The value for $C = 2$ is of the most interest, since it corresponds to a division of the material into two equal fractions. A convenient equation for use with *intermediate fractions* is

$$\triangle M = \frac{B}{C_2 - C_1}(C_1 \ln C_2 - C_2 \ln C_1).$$

Chapman's equation for *thermal diffusion* may be changed into a form which is similar, as follows:

$$\triangle M = K.B \ln \frac{T'}{T} \quad (21)$$

in which B has its usual value. Since K is about $\frac{1}{4}$, thermal diffusion, for any ordinary ratio of temperatures such as $\frac{1240°}{80}$, is a much weaker agent than ordinary diffusion, since this ratio causes only half the change of molecular weight for a cut of 2 as is given by the same cut when the latter method is used.

For *pressure diffusion*, such as that due to centrifugal force,

$$\triangle M = B \ln \frac{p}{p_o} \text{ (approximately).} \quad (27)$$

or $$\triangle M = \frac{(M_2 - M_1)^2 x_1 x_2}{2RT}(v^2 - v_o^2) = P(v^2 - v_o^2) = Pw^2(r^2 - r_o^2) \quad (28)$$

The equations for thermal and pressure diffusion, as given above, were developed in this laboratory by Mulliken.[89] Rayleigh's equation (1) was developed for the calculation of the diffusion of gases into each other, but it may be easily shown that it is also applicable to irreversible evaporation. Let x and y represent the number of mols of the light and heavy isotope, respectively, in the *heavy fraction* after the diffusion, and X and Y the initial mol numbers. Then

[89] *J. Am. Chem. Soc.*, **44**, 1033–51 (1922).

$$\frac{1}{C} = \frac{x+y}{X+Y} = \frac{X}{X+Y} r^{\frac{\mu}{v-\mu}} + \frac{Y}{X+Y} r^{\frac{\mu}{v-v}} \qquad (1)$$

where μ and v represent the diffusion coefficients of the light and heavy constituents, respectively. This is easily converted into the form

$$\frac{Q}{Q_0} = \frac{1}{C} = r^{\frac{v}{v-\mu}\left[1 + \frac{Y}{X+Y}(r-1)\right]} \qquad (2)$$

If it is assumed that the rates of diffusion of the gases vary inversely as the square roots of their molecular weights, this reduces to the following simple form:

$$\frac{1}{C} = r^{\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}\left[1 + h_0(r-1)\right]} \qquad (3)$$

in which h_0 represents the fraction of the heavy isotope $Y/(X+Y)$ in the initial mixture, and M_l and M_h are the molecular weights of the light and heavy components of the mixture.

66. RELATION BETWEEN THE ATOMIC WEIGHTS AND PERCENTAGES OF TWO ISOTOPES AND THE ATOMIC WEIGHT OF THE MIXTURE.

In order to calculate the cut necessary to produce a certain change in the atomic weight of a mixture of two isotopes, it is necessary to know the fraction of each in the mixture, and this may be calculated from the mean atomic weight and the atomic weights of the pure isotopes. Let h_0 and l_0 represent the initial fractions of the heavy and light isotopes, h and l the similar values necessary to produce the required enrichment (r), and M, M_h, and M_l, the molecular weights of the mixture, of the heavy, and of the light fractions.

Then

$$l \cdot M_l + (1-l) M_h = M$$

or

$$l = (M_h - M) / (M_h - M_l). \qquad (4)$$

Similarly

$$(1-h) M_l + h M_h = M$$

or

$$h = (M - M_l) / (M_h - M_l). \qquad (5)$$

Divide (4) by (5):

$$r = \frac{h/l}{h_0/l_0} = \frac{M - M_l}{M_h - M} \cdot \frac{M_h - M_0}{M_0 - M_l} \qquad (6)$$

By the use of Equations 3 and 6 the calculation of the cut necessary to produce any possible desired increase in atomic weight is very simple. It is obvious that the two equations may be combined into one.

$$\frac{Q_o}{Q} = \frac{1}{C} = \left[\frac{M-M_l}{M_h-M} \cdot \frac{M_h-M_o}{M_o-M}\right]^{\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}} \left[1+h_o\left(\frac{M-M_l}{M_h-M} \cdot \frac{M_h-M_o}{M_o-M}-1\right)\right]. \tag{7}$$

If we let k represent $\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}$ the "diffusion exponent," then the diffusion equation reduces to the simple form:

$$\frac{1}{C} = [1+h_o\,(r-1)] \times r^k. \tag{8}$$

The value of the diffusion exponent (k) as thus defined is -37.503 for the isotopic forms of hydrogen chloride provided the only isotopes have molecular weights 36.008 and 38.008, while for neon it has the value -21.488, provided the only isotopes have atomic weights 20 and 22. It may be noted that the values of the diffusion exponents are not very different from the mean molecular weights, but that this is not a general relation unless the isotopes differ in atomic weight by 2, is shown by the fact that the exponent for lithium, with atomic weights 6 and 7, is -13.48. The exponent for the isotopic forms of hydrogen bromide of molecular weights 80 and 82 (bromine of atomic weights 79 and 81) is -81.492. A convenient rule for keeping in mind the magnitude of the exponent is that it has a value equal to half a unit more than the mean of the molecular weights of the isotopes when the two molecular weights differ by 2. Thus for isotopes of atomic weights 223 and 225, the exponent is -224.5. Obviously the exponent has larger values when the difference between the isotopes is only 1, and smaller values when it is greater than 2. When the difference is 1 the exponent is equal to half a unit more than *twice* the mean of the atomic weights, and when it is 4, it is equal to half a unit more than *one-half* the mean.

Equation 8 may be put in the form

$$\frac{1}{C} = \left[1+l_o\,(r-1)\right] \times r^{k+1} \tag{9}$$

or $$\frac{1}{C} = r\frac{\sqrt{M_l}}{\sqrt{M_l}-\sqrt{M_h}}\left[1 + l_0(r-1)\right] = r^{k'}\left[1 + l_0(r-1)\right]. \qquad (10)$$

The numerical value of k' is always one unit less than that for k, and the mean of these two values is for two isotopes equal to the mean of the molecular weights when the molecular weight difference is 2, twice the mean of the molecular weights when this difference is 1, and one-half the mean of the molecular weights when this difference is 4, or

$$\frac{k+k'}{2} = \frac{M_l + M_h}{M_l - M_h} \qquad (11)$$

and $$k + k' = 1. \qquad (12)$$

67. ISOTOPIC MOLECULES AND ISOMERIC MOLECULAR ISOTOPES.

It is of considerable interest that the existence of isotopic atoms necessitates the existence of *isotopic molecules*, and that the number of the latter is very great. Thus zinc has 4 and chlorine has 2 known isotopes, which corresponds to the existence of 12 molecular isotopes of zinc chloride. Since tin has 8 isotopes, there are 40 molecular isotopes of $SnCl_4$. The number of isotopes of $SnBr_4$ is also 40, while for $SnBr_2Cl_2$ it is 72.

If an element containing mol-fractions x_1 and x_2 of two isotopes is combined into molecules containing n_e atoms each of this element, there will be $n_e + 1$ isotopic molecular species, whose mol fractions can be shown to be given by the successive terms of the expansion of $(x_1 + x_2)^{n_e}$. If the element has (s) instead of only two isotopes, the corresponding expression is $(x_1 + x_2 + \ldots + x_s)^{n_e}$, which gives $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ terms, corresponding to an equal number of molecular isotopes. If the compound contains atoms of several elements E, E', E'', ..., each having a set of isotopes, as E_1, E_2, ... E_s, for element E; E'_1, E'_2, ... $E'_{s'}$, for element E', etc., and if each element contains mol-fractions $x_1, x_2 \ldots x_s$; $x'_1, x'_2, \ldots x'_s$, etc., of its isotopic atomic species, then the mol-fractions of the various possible molecular species will be given [90] by the terms of the complete

[90] These expressions take account of all elements present in a compound, even if some of them contain only one isotope ($s = 1$). The factor $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ reduces to 1 in the latter case ($0! = 1$, by definition), so that it is necessary to consider only the elements in the molecule which contain isotopes.

expansion of $(x_1+x_2+\ldots\ldots x_s)^{n_e}\ (x'_1+x'_2+\ldots\ldots x'_{s'})^{n'_e}$ $(\ldots\ldots)\ (\ldots\ldots)\ldots$ The total number of terms, and so of molecular isotopes, is $\frac{(n_e+s-1)!(n'_e+s'-1)!(\ldots\ldots)!(\ldots\ldots)!\ldots}{n_e!n'_e!\ldots\ldots(s-1)!(s'-1)!(\ldots\ldots)\ (\ldots\ldots)}$. The composition of the molecular species to which any term refers is given by the particular x's occurring in that term, and their exponents. Thus $(x_1)\ (x_2)\ (x'_4)\ (x'_1)_2\ (x'_2)_4$ would be the mol-fraction of the molecular species $E_1E_2E'_4(E''_1)_2(E''_2)_4$. Since 2 isotopes each have been detected for chlorine and for bromine, and probably 6 for mercury, the number of isotopes of either $HgCl_2$ or $HgBr_2$, which accords with our present knowledge, is given by the expression $\frac{6!\ 3!}{1!\ 2!\ 5!\ 1!}=18$. The corresponding expression for $NiCl_2$ or $NiBr_2$ is $\frac{2!\ 3!}{1!\ 2!\ 1!\ 1!}=6$, since there are 2 isotopes of nickel.

Among compounds containing more than one isotopic element, there will often be instances of isotopes of equal molecular weight. For example, $MgCl_2$, under conditions [91] where its molecules exist as permanent entities, would contain 9 isotopes having molecular weights 94, 95, 96, 96, 97, 98, 98, 99, 100. For both $Mg^{24}Cl^{35}Cl^{37}$ and $Mg^{26}(Cl^{35})_2$ the molecular weight is 96, and for both $Mg^{24}(Cl^{37})_2$ and $Mg^{26}Cl^{35}Cl^{37}$ it is 98 (isobaric molecules).

When an isotopic element appears in an organic molecule, its isotopism not only results in numerous isotopic molecular species, but also in many cases introduces new position isomers. For example, C_6Cl_6 must have 7 molecular isotopes, of which all but $C_6(Cl^{35})_6$ and $C_6(Cl^{37})_6$ must exist in several isomeric forms, due to the presence of the two different substituents Cl^{35} and Cl^{37}. Again, $CH_3.CHCl.CH_2Cl$ must consist of 4 molecular species, the isotopes $CH_3.CHCl^{35}.CH_2Cl^{35}$, $CH_3.CHCl^{37}.CH_2Cl^{37}$, $CH_3.CHCl^{35}.CH_2Cl^{37}$, and $CH_3.CHCl^{37}.CH_2Cl^{35}$, the last two being isomeric forms of the same isotope.

New optical isomers are possible as a result of isotopism, if isotopic atoms, by virtue of their different *masses* alone, can act as different substituents to make carbon or other atoms asymmetric.

[91] *I.e.*, in the vapor state, or in solution in non-ionizing solvents.

(*To be continued.*)

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

A PIEZO ELECTRIC METHOD FOR THE INSTANTANEOUS MEASUREMENT OF HIGH PRESSURES.[1]

By J. C. Karcher.

[ABSTRACT.]

A NUMBER of circular quartz plates are cut from a quartz crystal so that an electric axis is perpendicular to the plane surface of the plates. These plates are stacked up condenser fashion with sheet metal electrodes. Electrodes collecting charges of like sign are connected to a common terminal. The two terminals are electrically connected to a ballistic galvanometer.

The stack of plates is subjected to the pressure to be measured by means of a piston which exerts a force perpendicular to the plane faces of the plates. When pressure is applied, a charge is liberated by the plates which flows through the galvanometer, causing a deflection. The galvanometer deflection is photographed on a rapidly-moving film. The pressure-time curve is the differential of the recorded deflection-time curve multiplied by the proper constant.

It has been found that the amount of charge liberated by the quartz plates is proportional to the pressure applied, for pressures up to 50,000 pounds per square inch. If the dynamic equation for the motion of the galvanometer is

$$Gi = K\frac{d^2\Theta}{dt^2} + D\frac{d\Theta}{dt} + U\Theta$$

where G is the dynamic constant of the moving system, K its moment of inertia, D the damping constant and U the restoring constant of the galvanometer. If the piezo electric current of the gage is C, then

$$\frac{dq}{dt} = C\frac{dP}{dt} = i.$$

If the time of duration "t" of the pressure phenomena is small compared to the period of the galvanometer, and if the

* Communicated by the Director.

[1] *Scientific Papers*, No. 445.

amount of damping on the galvanometer is small, then U and D will be small and

$$GC\frac{dP}{dt} = K\frac{d^2\Theta}{dt}$$

$$P = \frac{K}{GC}\frac{d\Theta}{dt} + C' \; (P = O \text{ when } \frac{d\Theta}{dt} = U. \therefore C' = 0)$$

$d\theta/dt$ is determined by reading slopes on the recorded deflection-time curve. K/GC is determined by calibrating the gage in a testing machine. The gage is subjected to a known load P_0 and the galvanometer deflections θ_0 is read, then

$$\frac{K}{GC} = \frac{P_0 T}{2\pi(1 + \lambda/2)\Theta_0}$$

where λ is the logarithmic decrement of the galvanometer. Computations are made to show the sensitivity of the system.

Actual pressure measurements in guns have been made with several gages. A comparison with other data obtained simultaneously indicates that the performance of the gage is in entire accord with the theory developed. Results are not available for publication.

SPECTROPHOTOELECTRICAL SENSITIVITY OF ARGENTITE (Ag_2S).[1]

By W. W. Coblents.

[ABSTRACT.]

THE present paper, considered in connection with some previously published data, represents a study of the effect of crystal structure upon photoelectrical sensitivity, as observed in silver sulphide, Ag_2S, in the isometric form argentite, and in the orthorhombic form, acanthite.

Experimental data are given on the effect of temperature, of the intensity of the radiation stimulus, and of mechanical working of the material, upon the spectrophotoelectrical sensitivity of argentite. These observations are then compared with similar data, previously published, on acanthite.

Argentite reacts slightly photoelectrically to radiations of wave-lengths 0.5 to 1.1μ, followed by a sharp, fairly symmetrical maximum at 1.35μ. In contrast with this is acanthite, which reacts quite strongly to radiations at 0.5 to 1.0μ followed by an

[1] *Scientific Papers*, No. 446.

unsymmetrical maximum at 1.35μ. Both minerals react selectively to ultra-violet rays.

At low temperatures, the intrinsic photoelectrical sensitivity of argentite is greatly increased and the maximum shifts to the short wave-lengths—to 1.1μ as compared with 1.2μ for acanthite, under similar conditions.

The photoelectrical reaction of argentite differs from that of acanthite in being free from an induced photo-negative polarization.

In argentite, as previously observed in acanthite (also molybdenite, etc.), increasing the intensity of the radiation stimulus produces a more rapid reaction in the long wave-lengths than in the short wave-lengths, with a consequent shift of the maximum of the photoelectrical sensitivity curve toward the long wave-lengths.

Hammering the crystals of argentite and acanthite into thin, pliable, plates lowers the intrinsic photoelectrical sensitivity. The position of the maximum of spectrophotoelectrical sensitivity of the worked samples is less affected by changing the temperature than obtains in the natural crystalline state; and it is practically the same for these two minerals, at low temperatures. From this it appears that aside from the effect of crystal structure, silver sulphide has a photoelectrical response spectrum characteristic of this substance.

From a comparison of the spectrophotoelectrical reactions of these two crystal forms of silver sulphide under various conditions it appears permissible to conclude that crystal structure has a marked effect upon spectrophotoelectrical sensitivity.

THE DECARBURIZATION OF FERRO-CHROMIUM BY HYDROGEN.[1]

By Louis Jordan and F. E. Swindells.

[ABSTRACT.]

THE recently developed "rustless" iron may be considered as a stainless steel from which the carbon has been largely eliminated. The carbon content of rustless iron is in the neighborhood of, or less than, 0.1 per cent. In order to produce an iron alloy containing as high as 12 per cent. chromium and still keep the carbon content as low as indicated, it is necessary to use ferro-

[1] *Scientific Papers*, No. 448.

chromium lower in carbon than the more common commercial grades bearing 4 to 8 per cent. carbon. Carbon-free ferro-chromium made by alumino-thermic methods is available, but at prices which are too high to allow its extended use in producing rustless iron.

Various procedures for decarburizing high-carbon ferro-chromium have been described in a number of patents. The decarburization of ferro-chromium by means of hydrogen has been suggested. The decarburization of cast iron and steels by heating in hydrogen at temperatures between 400° and 1200° C. has been described previously. Tests carried out on 60 per cent. ferro-chromium containing 8 per cent. carbon showed that there was a slow decarburization of the powdered ferro alloy by dry hydrogen between 1100° and 1350° C. The removal of carbon was more rapid just above than just below the melting point of the alloy. The most rapid decarburization was secured by bubbling hydrogen through molten ferro-chromium at approximately 1500° C. Under these conditions nearly 1 per cent. of carbon was removed from the alloy in four minutes as compared with four hours required to reduce the carbon 1.6 per cent. at a temperature just below the melting point of the alloy. The most promising condition for refining high-carbon ferro-chromium by this method is probably blowing the molten alloy with a blast of hydrogen in a converter.

RADIO-FREQUENCY AMPLIFIERS.[4]

By P. D. Lowell.

[ABSTRACT.]

ELECTRON tube amplifiers now form an essential part of all but the most simple radio receiving sets. By the use of a good amplifier a feeble signal may be made loud enough to be heard throughout a large room, and a signal which is so feeble as to be inaudible may be made loud enough to be clearly read. Amplifiers are in fact necessary to receive distant stations, or when using coil antennas. The received radio-frequency current may be amplified before it is rectified by a detector tube; this is called "radio-frequency amplification." Or the rectified output of the detector tube may be amplified; this is called "audio-frequency

[4] *Scientific Papers*, No. 449.

amplification." Persons desiring an elementary discussion of amplification may refer to the "Principles Underlying Radio Communication," Signal Corps Radio Communication Pamphlet No. 40.

An amplifier which has one tube used as a detector and two tubes used as amplifiers is said to have two *stages* of amplification. The simplest amplifiers have one or two stages of audio-frequency amplification. If it is desired to use four or more stages of amplification, it is necessary to use radio-frequency amplification as well as audio-frequency amplification. If the attempt is made to use more than three stages of audio-frequency amplification, serious disturbances are likely to be caused which will result in "howling" noises in the telephone receivers; these noises may be caused by regenerative effects. It is often advantageous to use radio-frequency amplification even if only one stage of audio-frequency amplification is used. A certain minimum signal is required for good operation of a detector tube, and if only a very feeble signal is being received, it is necessary that radio-frequency amplification be used in order that a signal of proper strength be delivered to the detector tube.

Radio-frequency amplification can make clearly audible a signal from a distant station which without such amplification is entirely inaudible. In a properly designed amplifier, the use of radio-frequency amplification often improves considerably the ratio of signals to strays. Radio-frequency amplification alone will not, however, give a signal strong enough to operate a loud-speaker, since the detector tube does not have sufficient output to operate a loud-speaker. If a loud signal is desired audio-frequency amplification should be used.

The small coil antennas used in direction finding work receive only a very feeble signal, and it is necessary to amplify these feeble signals many times if it is desired to do accurate direction finding work. This is particularly true if the minimum method of direction finding is used. Methods of direction finding are discussed in Bureau of Standards Scientific Paper No. 428, by F. A. Kolster and F. W. Dunmore, "The Radio Direction Finder and Its Application to Navigation."

A multistage amplifier consists of a number of electron tubes connected in suitable circuits. Each tube amplifies the signal impressed on its grid circuit and delivers the amplified signal from

its plate circuit. The output or plate circuit of one tube is coupled to the input or grid circuit of the next tube by any one of several methods. It is important that efficient methods be used for transferring the signal energy from the plate circuit of one tube to the grid circuit of the next tube.

There are three methods by means of which the electron tubes may be coupled together so as to give amplification at radio frequencies; first, resistance coupling; second, tuned plate coupling; and third, transformer coupling.

With resistance coupling, it is customary to connect in the plate circuit of the first amplifier tube a non-inductive resistance of about 80,000 ohms, having as low a distributed capacity as possible, and to connect a condenser of about 0.0005 microfarad capacity from the plate of this tube to the grid of the next tube. The radio-frequency variations of the current in the plate circuit of the first tube cause corresponding variations in the voltage across the resistance and hence radio-frequency variations in the potential of the grid of the second tube. This method is, however, limited to amplification of relatively low radio frequencies, and will not usually give satisfactory results on frequencies much above 150 kilocycles per second with the tubes at present ordinarily available.

In the second method, tuned plate coupling, the plate circuit of the first tube is actually tuned to the signal frequency either by means of an inductance shunted by a variable condenser, or by a continuously variable inductor, inserted in series with the plate circuit.

The circuit is similar to the resistance-coupled circuit except that the coupling resistance is replaced by either a continuously variable inductor, or by an inductance shunted by a variable condenser. A condenser permits the radio-frequency currents to flow from this plate to the grid of the next tube as in the resistance-coupled method. The tuned plate method is more efficient than resistance coupling at frequencies above 150 kilocycles per second.

The third method, transformer coupling, is the most efficient and therefore most desirable, and it is this method for which circuits were developed and which is discussed in this paper.

In all the circuits of a radio-frequency amplifier it is necessary to keep all capacities as low as possible. It is therefore necessary to use transformers whose windings have small distributed capa-

city, and to use electron tubes having small capacities between the elements.

It has been found that either air-core or iron-core transformers may be used for coupling the output circuit of one tube to the input circuit of the next. The air-core type gives more amplification per stage, but on the other hand, is responsive to only a narrow band of frequencies owing to the low effective resistance of its windings.

The iron-core type, while not giving as much amplification per stage, will allow amplification over a much broader band of frequencies.

However, a special form of air-core transformer has been developed for radio compass work, which will respond to signals on wave-lengths from 600 to 1000 metres by means of a simple and quick adjustment.

The coils of this air-core transformer were wound with No. 38 B. & S. gauge single-silk-covered copper wire in the form of a pancake or flat doughnut, as it is sometimes called, and are impregnated with insulating varnish to make them self-supporting. The wire was wound in a manner similar to the so-called "honeycomb" coils, or, as the British call it, a "basket" winding.

Two of the coils coupled together constitute an air-core radio-frequency transformer, one coil being connected in the plate circuit of one tube and another connected in the grid circuit of the succeeding tube, in the usual manner.

Several six-stage amplifiers have been made, utilizing iron-core radio-frequency coupling transformers, and have given very good results.

In constructing an iron-core transformer, the primary and secondary windings are wound on a square insulating tube in two single layers, side by side. A core made up of silicon steel laminations about the thickness of a piece of tissue paper is placed inside the insulating tube.

The construction of a radio-frequency amplifier is quite a difficult task and requires no little amount of patience and resourcefulness, but when constructed properly is, of course, extremely useful for the reception of signals with a coil aerial. The coil aerial permits the elimination of undesired and interfering signals by rotation of the coil to the point where the unwanted signals drop out.

AN ELECTRON TUBE AMPLIFIER USNG 60-CYCLE ALTERNATING CURRENT TO SUPPLY POWER FOR THE FILAMENTS AND PLATES.[5]

By P. D. Lowell.

[ABSTRACT.]

ELECTRON tube amplifiers form an important part of practically all radio receiving sets now, except the most simple types. Such amplifiers are in fact necessary to receive distant stations, or when using coil antennas. For good operation, amplifier tubes require for the filament a source of voltage of very constant value (usually about 6 volts) and for the plate a source of voltage of from 40 to perhaps 300 volts. The filament voltage is usually supplied by storage cells, and the plate voltage by dry cells. The maintenance of these cells in operating condition, especially the storage cells, is often a source of much difficulty and annoyance. The storage cells are necessarily bulky and heavy, require constant attention to maintain proper charge and density of electrolyte, and give off injurious acid or other fumes. The development of an amplifier which can be supplied from the ordinary 110-volt a.c. lighting mains is of considerable practical importance, since it would eliminate the practical difficulties of maintaining storage cells. The amplifier using such a.c. supply has the important advantages of reliability, convenience, and cheapness both in first cost and operating cost.

Such an amplifier using five stages of amplification has been developed at the Bureau of Standards. There are three stages of radio-frequency amplification and two stages of audio-frequency amplification. This paper describes this amplifier briefly.

The voltage for the filaments is obtained from one winding of a 60-cycle transformer having four windings. The primary is connected to the 110-volt 60-cycle a.c. lighting supply. The grid circuits, instead of being connected directly to one terminal of the filament supply, are connected to an intermediate point between the filament supply terminals through the medium of a slide-wire voltage divider, the ends of the voltage divider being across the filament supply and the grid circuits being connected to the sliding contact through a one microfarad condenser shunted by a one megohm leak resistance. One voltage divider is used

[5] *Scientific Papers*, No. 450.

for the grids of the radio-frequency tubes and one for the grids of the audio-frequency tubes. By adjusting the sliders of the voltage divider, the grids may be brought to a value of voltage which is constant with respect to the changing voltage of the filament, thereby reducing the a.c. hum. The one microfarad series condensers serve to allow the grids to assume a favorable condition for amplifying. It was found to be more desirable to replace the condenser and leak resistance in the grid leaks of the audio-frequency tubes with a 10-volt negative dry battery which gave better amplification with less hum.

It was found that a crystal detector gave much better operation with less hum than a tube detector because the former can be entirely insulated from the a.c. power circuit and picks up less hum than the tube detector.

Plate voltage is supplied from another winding of the 60-cycle transformer, the a.c. voltage being rectified by means of a two-electrode electron tube and smoothed out by large condensers to make it suitable for use on the plates of the amplifier tubes. The paper gives diagrams of various circuits used in the course of development and the final circuit employing five amplifier tubes.

This final circuit gives good amplification, with a slight residual hum which is not great enough to be objectionable when receiving signals of ordinary readable strength. The residual hum is of course more objectionable when extremely weak signals are being received. Radio telephone music and conversation are clearly reproduced.

The amplifier was operated under normal conditions using the usual sources of direct-current supply, and then switched over to alternating-current supply. This comparative test showed the a.c. supply to give as good amplification as the d.c. supply, although the set was slightly more sensitive to weak signals when batteries were used, on account of the interference caused by the hum when used on a.c. supply.

For the reception of damped waves, the amplifier as constructed operated most satisfactorily for frequencies from 400 kilocycles to 1500 kilocycles per second (750 to 200 metres). This frequency range was determined by the working range of the radio-frequency transformers used. By using suitable radio-frequency transformers, it is expected that the amplifier will be effective for the reception of damped waves for frequencies as

low as 30 kilocycles (10,000 metres). This amplifier has also been found effective for the reception of undamped waves, when used with a separate heterodyne.

The use of a loud-speaking telephone receiver such as the "Magnavox" was made possible by applying to the field coil of the loud-speaker an alternating current rectified by a "Tungar" rectifier tube. The impedence of the field coil was sufficient to smooth out the pulsating current to such an extent that the hum was not annoying. It was also advantageous to couple the loud-speaking reproducer circuit to the plate circuit of the last amplifier tube by means of a one-to-one ratio telephone transformer with a 0.02 microfarad condenser in series with the telephone circuit.

SPECTROPHOTOELECTRICAL SENSITIVITY OF BOURNONITE AND PYRARGYRITE.[6]

By W. W. Coblentz and J. F. Eckford.

[ABSTRACT.]

THE present paper, considered in connection with previously published data on proustite (Bureau of Standards Scientific Papers, No. 412), represents a study of the effect of chemical constitution upon spectrophotoelectrical sensitivity.

Experimental data are given on the effect of temperature and of the intensity of the radiation stimulus upon the photoelectrical sensitivity of the minerals bournonite and pyrargyrite, in the spectral region extending from 0.3μ in the ultra-violet to 2μ in the infra-red.

The spectrophotoelectrical reaction curve of bournonite is entirely different from that of the constituent sulphides of copper and lead (which are not photo-sensitive) and of antimony which has its photoelectrical sensitivity confined principally to a band at 0.77μ in the extreme red. On the other hand, bournonite has a high spectrophotoelectrical sensitivity extending from the extreme violet to 1μ in the infra-red, with two wide, ill-defined maxima in the region of 0.55μ and 0.95μ respectively.

On lowering the temperature the intrinsic spectrophotoelectrical sensitivity of bournonite is greatly increased and the maxima shift towards the short wave-lengths. The maximum in the violet usually remains the more intense at the lowest temperatures.

[6] *Scientific Papers*, No. 451.

The spectrophotoelectrical reaction of the mineral pyrargyrite, which is a double sulphide of silver and antimony, is entirely different from that of the constituent sulphides of silver and of antimony, which also exhibit photosensitivity.

At 22° C. the photoelectrical reaction of pyrargyrite consists of a wide unsymmetrical maximum in the ultra-violet, with a weak, ill-defined maximum in the region of 0.63μ.

At low temperatures, – 165° C., pyrargyrite reacts electrically to radiations of all wave-lengths extending from the extreme ultra-violet to 1.5μ in the infra-red; but the greatest photoelectrical reaction is localized in the band at 0.63μ.

There is a great similarity in the spectrophotoelectrical and chemical properties of pyrargyrite (silver-antimony sulphide) and of proustite (silver-arsenic sulphide). In a general way, the foregoing properties of photoelectrical reaction spectra are analagous to properties of absorption spectra, as affected by chemical constitution, from which it appears that perhaps ultimately the two phenomena may be traced to a common source within the molecule.

THE PREPARATION OF IRON-CARBON-MANGANESE ALLOYS AND THE EFFECTS OF CARBON AND MANGANESE ON THE MECHANICAL PROPERTIES OF IRON.[1]

By R. P. Neville and J. R. Cain.

[ABSTRACT.]

THIS paper describes the preparation and mechanical properties of a series of very pure alloys of electrolytic iron, carbon, and manganese, whose compositions were so chosen as to bring out the specific effects on pure iron of: (1) additions of carbon; (2) additions of manganese; and, (3) additions of carbon and manganese together in varying relative proportions. The maximum amount each of carbon and manganese in each series was about 1.5 per cent.; the minimum, 0 per cent., or pure iron.

The alloys were made in three-pound ingots by melting electrolytic iron in an electric vacuum furnace, in a crucible of pure magnesia, to which the carbon and manganese were added after fusion of the iron. From these ingots tensile test specimens were made and tested in the annealed condition.

[1] *Scientific Papers*, No. 453.

Data are tabulated and grouped so as to bring out the effects of each element. From these data curves were constructed which show graphically the effects of carbon and of manganese on the mechanical properties of the alloys.

Carbon increased the ultimate strength of the iron at an average rate of about 1000 lbs. per sq. in. for each 0.01 per cent. carbon, up to a content of about 0.85 to 1.0 per cent., the rate increasing with the increase in manganese. The proportionate increase in Brinell hardness was about the same as that for ultimate strength. The proportional limits were less affected by carbon than were the ultimate strengths. Elongation and reduction of area were rapidly reduced as the carbon increased.

Manganese, in the absence of carbon, had very little effect on the mechanical properties of iron. With the addition of carbon its effect was increased proportionately with the carbon content, raising the ultimate strength from 90 to 250 lbs. per sq. in. for each 0.01 per cent. manganese. Brinell hardness was increased in about the same manner. The proportional limit was increased more by manganese than was the ultimate strength. The effect of manganese on ductility was negligible.

Further Studies on the Electron Theory of Solids. SIR J. J. THOMSON. (*Phil. Mag.*, October, 1922).—The arrangement of atoms and electrons is pretty well known for calcium. From consideration of the electrical forces involved Sir J. J. Thomson computes its compressibility to be 5.9×10^{-12}, which agrees with Richards' measured value of 5.5×10^{-12}. In the case of the diamond the calculated value of the compressibility agrees quite closely with that of Adams but is only one-third of that found by Richards.

The old method of using the electrons to explain the transfer of heat and of electricity was to consider them as moving about rather freely within the conductor. Now their motion is regarded as far less free. In a metal all the electrons occupy definite positions in relation to the atoms and a whole series of them lie in a row. By the motion of such a row of electrons the author proceeds to show how both heat and electricity are transferred and he succeeds so well that he arrives at a formula that embodies the Wiedemann-Franz law according to which "the ratio of the thermal to the electrical conductivity should at the same temperature be the same for all metals, and at different temperatures should be proportional to the absolute temperature." And this is not all, for he furnishes an explanation of the super-conductivity of lead at low temperatures, discovered by Kammerlingh Onnes. G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

NOTE ON THE RELATION BETWEEN SENSITIVENESS AND SIZE OF GRAIN IN PHOTOGRAPHIC EMULSIONS.[1]

By S. E. Sheppard and A. P. H. Trivelli.

In confirmation of Mr. Renwick's emulsion experiments an experiment reported shows that coarse-grained emulsions are not always more sensitive than fine-grained ones, although in the same emulsion statistically there is a probability of greater sensitivity for larger grains. From a theoretical treatment of the subject the conclusion is drawn that the catalytic effect of silver nuclei depends on orientation in relation to the silver halide crystal lattice, and that in turn on the exposure. It is noted that the difference in effect on clumps of grains of developers of high and low reduction potentials should be considered in the experimental work.

QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE.[2]

By L. Silberstein.

After a short introduction concerning the structure of the photographic plate, the assumption is made that light consists, either entirely or in part, of discrete energy parcels or light darts, each containing a quantum of energy, and that a silver halide grain is affected, *i.e.*, made developable whenever it is hit by one or more light darts of a sufficiently high frequency or of a sufficiently short wave-length. With these assumptions the problem of the production of the latent image is reduced to a problem in probabilities and its solution gives the percentage number of grains affected as an exponential function of the size (area) of the particular class of grains and of the number of light quanta thrown upon the plate. The integral effect ranging over any finite interval of sizes is then deduced. Further the dependence

* Communicated by the Director.

[1] Communication No. 128 from the Research Laboratory of the Eastman Kodak Company and published in *Phot. J.*, November, 1921, p. 400.

[2] Communication No. 139 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, July, 1922, p. 257.

of the number of affected grains upon wave-length is discussed in connection with a possible finite cross-section of the light darts. Finally the aforesaid exponential formula, supplemented by a term corresponding to a finite section of the light missiles, is tested on a series of thirty-three microphotographic observations on grain clumps made for this purpose by Trivelli and Righter. Each clump of the special experimental emulsion being considered as a single photographic unit or target, of area equal to the sum of the areas of its component grains, the theoretical percentage numbers of clumps affected by a unique exposure are found to agree very accurately with the observed ones over a range of sizes from 0.75 – 25.0 square microns, the corresponding percentage numbers of units affected ranging for the thirty-three classes, from 16 to full 100 per cent. These results are tabulated numerically and represented by a graph. The tests afforded by other experiments and some further theoretical deductions will be published shortly in the same journal.

ON THE MUTUAL INFECTION OF CONTIGUOUS SILVER HALIDE GRAINS IN PHOTOGRAPHIC EMULSIONS.[2]

By A. P. H. Trivelli, F. L. Righter, and S. E. Sheppard.

THIS paper gives a brief discussion of the results obtained by T. Svedberg when using a special emulsion furnished by F. F. Renwick and a ferrous oxalate developer. It is pointed out that the results of Svedberg directly contradict results obtained by Svedberg's method in this laboratory. A description of the work with photomicrographs, curves and resultant data is given. The wide deviation in results obtained in the two curves is thought to be due largely to the great difference in the type of emulsion used.

Ratio of Mass to Weight for Bismuth and Aluminium. H. A. WILSON. (*Phys. Rev.*, July, 1922).—Brush has described experiments which seem to show that the ratios between mass and weight are different for different substances, and that this is especially the case with bismuth and aluminium. Now from the Rice Institute comes a fresh determination for the same two substances by the method of Eötvös. The conclusion is that the acceleration is the same for both elements to within one part in a million. G. F. S.

[2] Communication No. 146 from the Research Laboratory of the Eastman Kodak Company and published in *Photo. J.*, September, 1922, p. 407.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

PROGRESS IN THE PHYSICAL CHEMISTRY OF GELATIN.[1]

By C. R. Smith.

[ABSTRACT.]

CHEMICALLY pure gelatin cannot be said to have been prepared as yet. Recent studies of the physico-chemical properties of gelatin, including the mutarotation, osmotic pressure, and swelling, define the quality of material used. "Ash-free" gelatin, with interesting properties, has been prepared and used in experimental work where small and unmeasured amounts of electrolyte impurities nullify the results.

The osmotic pressure and swelling of gelatin sols and gels in acids and alkalies has been shown to be ionic phenomena dependent on the extent of combination, ionization, valency, and quantity of ions opposite in charge to the gelatin present. Recent work has been considered as proving the distribution of acids, bases, and salts between gelatin and water separated by a semipermeable membrane to follow Donnan's theory of membrane equilibrium. The writer, however, points out certain fundamental requirements of this theory which have not yet been verified.

THE INFLUENCE OF ATMOSPHERIC HUMIDITY ON THE STRENGTH AND STRETCH OF LEATHER.[2]

By F. P. Veitch, R. W. Frey and L. R. Leinbach.

[ABSTRACT.]

THE effect of humidity on the physical properties of certain fibrous materials such as paper has been recognized for some time, as is shown by the testing of this material under controlled conditions of temperature and relative humidity. It begins to appear that such practice will be necessary in testing leather, especially for research studies. For an ungreased, vegetable-tanned leather a surprisingly great effect from humidity is shown, and it is

* Communicated by the Chief of the Bureau.

[1] Published in *J. Am. Leather Chemists' Assoc.*, **17**, Oct., 1922, 508.

[2] Published in *J. Am. Leather Chemists' Assoc.*, **17**, Oct., 1922, 492.

probable that on most, if not all, leathers there is an influence too great to be safely ignored.

For a comparison of two different relative humidities a section of leather from the prime location in the side was cut into 180 test pieces. Alternate pieces were tested at one condition and the remainder at the other. Charts, prepared to show the data for the individual test, show incidentally the marked lack of uniformity in the physical properties of a given piece of leather. The test pieces were conditioned, weighed, and tested within a special constant temperature—constant humidity room, automatically controlled twenty-four hours of the day. The temperature was kept at 70° F. throughout the experiments.

The following grand average results were obtained: For an increase of 20 per cent. relative humidity, from 35 to 55 per cent., the increase in tensile strength was 12.9 per cent. and in elongation 15.7 per cent. For an increase of 40 per cent. relative humidity, from 35 to 75 per cent., the gain in tensile strength was 42.3 per cent. and in elongation 53.1 per cent. The increases, while not directly proportioned to the increase in relative humidity, are very closely parallel to the percentage gain in moisture.

A COMPARATIVE STUDY OF SPOILAGE IN SALMON.[2]

By Albert C. Hunter.

[ABSTRACT.]

IN a study of the spoilage of mature humpback salmon caught on the spawning migration in Puget Sound and of humpback salmon taken from the spawning grounds of the Green River, it was found that a somewhat different rate and a different type of spoilage take place in the two groups of fish. The difference in the total number of bacteria in the gills, in the flesh of the back and belly, in the pyloric coca, in the stomach, and in the intestines of the two groups of salmon was not great enough to explain the difference in the rate of spoilage. A study of the aerobic and anaerobic organisms representing the bacterial flora of these decomposing salmon indicates that practically the same bacteria are responsible for the decomposition of both groups of salmon.

In addition to the bacteria which have been previously described by the author as being responsible for the decomposition

[2] Published in *Am. Food J.*, 17, Sept., 1922, 19.

of salmon, several sporulating anaerobes were isolated from the decomposing fish.

It is probable that the difference in the rate and type of spoilage in the two groups of salmon is due to a marked difference in chemical composition of the fish, rather than to any appreciable difference in bacterial flora.

SOME EXPERIMENTS WITH A BORIC-ACID CANNING POWDER.[4]

By Ruth B. Edmondson, Charles Thom and L. T. Giltner.

[ABSTRACT.]

A BORIC-ACID canning powder was examined in the Bureau of Chemistry. In the quantity recommended it exerted a selective antiseptic action toward certain molds and members of the aerobic group of microörganisms in test-tube experiments. These groups are not responsible for spoilage in properly processed cans or jars, and may therefore be disregarded for the present purposes. The powder in the quantity recommended for canning had no inhibitory effect on representative members of the anaerobic spore-forming group, especially the toxin-forming *B. botulinus*, which has recently been responsible for many deaths from food poisoning.

In the practical canning experiments the use of the powder for acid products was shown to be an unnecessary and wasteful practice, since material packed without the powder kept as well as that packed with it. Its use with the more or less neutral vegetables showed that the powder plus the inadequate heating recommended was not sufficient to preserve the materials or to prevent the production of toxin in them by *B. botulinus*.

Influence of Changes in the Radiation and Activity of the Sun Upon Conditions on the Earth. G. ANGENHEISTER. (*Verh. Deutschen Physik. Gesell.*, Dec. 31, 1921.)—When the number of sun spots is at its maximum, the sun itself is hotter than usual but the earth, strange to say, is cooler.

The evidence for a higher temperature on the sun at that time is:

(*a*) Abbot's determination that the solar constant is then a maximum. There is a difference of 2½ per cent. between its maximum and its minimum values.

(*b*) In general the distribution of brightness over the disc of the

[4] Issued as U. S. Dept. Agr. Cir. 237, Aug., 1922.

sun corresponds to what would be expected in the case of equilibrium in radiation. At sun spot maximum, however, there is a greater contrast between the appearance of the circumference and the middle of the disc, and the appearance approaches that which would accompany adiabatic equilibrium in the atmosphere of the sun. There are, then, stronger vertical movements. The cooler outer layers sink and are replaced by hotter masses. Thus the sun looks hotter and really radiates more energy.

(*c*) The brightness of Jupiter and of Enke's comet varies in an eleven-year period and is greatest at sun spot maximum.

Similarly the mean temperature of the earth follows the eleven-year sun spot period, but it is at its minimum just when the number of spots is greatest. Thus when the sun radiates most the earth is coolest. True the difference is not great, as the amplitude of the eleven-year temperature is only .5° C. at continental stations. The observations at Samoa, extending over thirty years, show the same thing precisely, though with a little larger amplitude.

Why is the earth cooler when the sun has its highest temperature? The wind records at Samoa likewise exhibit an eleven-year periodicity. At the time of sun spot maximum the trade winds are 10 per cent. more frequent than at the time of minimum. The influx of cooler air from higher latitudes is greater at the sun spot maximum, and the temperature of Samoa is lowered. Moreover the frequency of cirrus clouds in like manner displays the familiar eleven-year course, which has its maximum at the time of sun spot maximum. Thus at that time the albedo of the earth grows larger and more energy is sent back into space. The atmosphere absorbs .05 calorie per square cm. less in a minute, and the mean temperature of the earth drops a fraction of a degree. G. F. S.

Anemometer Investigations. (*U. S. Department of Agriculture Clip Sheet No. 225.*)—Through studies conducted by the Weather Bureau with the coöperation of the Bureau of Standards, much information useful in the design and construction of anemometer instruments for measuring wind velocities has been obtained. The relation between cup movement and actual wind movement, heretofore known confidently to about 50 miles an hour, is now known to 113 miles an hour.

Tests on about 30 instruments of various dimensions, proportions, and weights have been made in the wind-tunnels of the Bureau of Standards at velocities ranging from 5 to 60 metres per second. Certain of the instruments tested in the wind-tunnels have been taken to Mount Washington, N. H., for comparison in the very high natural winds prevailing there. When these free-air comparisons are completed and the data have been analyzed, an improved standard anemometer recording true velocities will be developed and corrections determined for records of velocity already compiled.

NOTES FROM THE U. S. BUREAU OF MINES.*

FUSIBILITY OF ASH FROM COALS OF THE UNITED STATES.

By W. A. Selvig and A. C. Fieldner.

THE Bureau of Mines has made a general survey of the "fusing" or "softening" temperatures of the ash from coals in the United States. Data on the fusibility of coal ash should be of considerable value to the coal consumer, mainly in connection with the troublesome formation of clinker resulting from the melting of the ash constituents in burning coal. When used together with the large number of coal analyses published by the bureau, it will assist the consumer in comparing different coals and in selecting the coal best adapted to his purpose.

The ash is the incombustible residue after complete combustion, and is derived from the inorganic mineral constituents. These are (1) inherent impurities in intimate mixture with the coal substance, (2) impurities such as clay, shale, pyrite, and calcite that are present as partings, layers, or nodules in the coal bed, and (3) fragments of roof or floor mixed with the coal in mining.

Coal ash varies so widely in chemical composition that no typical composition can be given, but generally falls within the following limits: Silica, 40 to 60 per cent.; alumina, 20 to 35 per cent.; iron oxides, 5 to 25 per cent.; lime, 1 to 15 per cent.; magnesia, 0.5 to 4 per cent., and alkalies, 1 to 4 per cent. The fusibility depends on several factors, such as ratio of bases to silica present, the particular bases, and the percentage of alumina. For example, ash extremely high in silica or in bases is not readily fusible. Ash low in iron is usually so high in silica that it is not readily fusible. Ash of coals high in pyrite contains much iron, and is likely to form clinker, the iron converting to ferrous oxide which unites with silica to form easily fusible silicates.

Some coal ash is so infusible that little clinker is formed, and ash slightly fusible often forms a porous, spongy clinker that does not obstruct flow of air through the fuel bed and is easily

* Communicated by the Director.

removed. Ash with a low fusing temperature, say 2100° F., may become quite fluid and spread out in a thin sheet, obstructing flow of air and localizing the heat in the fuel bed.

In general, the softening temperature of ash from coals in the United States ranges from 1900° to 3100° F., and may be classed as (1) refractory ashes, softening about 2600° F.; (2) ashes of medium fusibility, softening between 2200° and 2600° F., and (3) easily fusible ashes, softening below 2200° F.

Further details will be found in Bulletin 200 recently issued by the bureau.

ARC REGULATION IN ELECTRIC FURNACES AND PILOT LIGHT CONTROL.

By C. E. Sims.

In any furnace where two or more electrodes are used, one of the main problems in operation is the proper regulation of the electrodes. There are available a number of automatic control systems which, when functioning properly, give excellent regulation and an even, well-balanced load. These are expensive, however, and for small furnaces are often impractical, so that a large proportion of the furnaces are hand-operated.

An apparatus devised in the bureau's laboratory and used on an experimental single-phase furnace furnishes an accurate and sensitive control, and can be home made at low cost.

Two 40-watt tungsten bulbs are set upright on a shelf near the meter board and in full view from the hand controls. Each lamp is connected to one electrode (or bus bar); both lamps have a common connection to the metal bath in the furnace. Usually all that is necessary is to connect them to the shell of the furnace, but if that does not work, a steel bar can be buried in the hearth. In operation the brilliancy of the filament will vary with the drop in potential between the electrode and the bath. A lamp of this type will glow dull red at 15 volts and will safely stand surges up to 125 volts. When the power is on and no arc has been drawn the lamps will simply be in series across the bus bars and will glow with equal brilliancy. When current is flowing through the furnace they are lighted equally only when both arcs are exactly the same, that is, have the same length and, therefore, the same resistance. The slightest change in either arc is quickly and

accurately indicated by the lamps. If one electrode should touch the bath its pilot light would instantly go black. These lights, therefore, show the exact position of the electrodes at all times. For three-phase operation it is necessary merely to add one more lamp.

A more detailed account is presented in a report issued by the bureau in mimeograph form.

THAWING FROZEN GRAVEL IN PLACER MINING.

By Charles Janin.

The working of frozen gravels, a special problem in placer mining, has received much attention in Alaska and the Yukon Territory. The expense of thawing with steam points, the chief method of thawing frozen gravel for drift, surface mining, or dredging operations, has prevented the working of the lower-grade gravels in the frozen areas. About 1915, different persons started experimenting with an entirely new plan for softening the gravel. Water at natural summer temperature was applied by means of holes drilled through the frozen muck and gravel to bedrock, with satisfactory results. The method was taken up in the Dawson field by the Yukon Gold Company and the Canadian Klondike Company; at Nome, by the Alaska Mines Corporation, on Candle Creek by Edward Pearce, and others. While there is much to be learned regarding its practical application, it has passed the experimental stage and is proving of great value to the gold-mining industry.

Its successful application where water is obtainable under pressure without pumping will make large areas of low-grade ground available for dredging, and ground that previously has been considered of little value now will be of economic importance.

Details are presented in Technical Paper 309, "Recent Progress in the Thawing of Frozen Gravel in Placer Mining," published by the Bureau of Mines.

The Effect of Nascent Hydrogen on Hardening Steel Magnets. John Coulson. (*Phys. Rev.*, July, 1922).—Fifty or more steel bar magnets, 14.4 cm. long, were quenched to glass hardness at 850° or were hardened at 700°. They were then magnetized to saturation inside of a solenoid. After this they were alternately

heated and cooled until no further change in the magnetic moment was observable. Finally each magnet was made the cathode in an electrolytic cell containing a solution of sulphuric acid. The current, kept at two amperes, caused the evolution of nascent hydrogen upon the surface of the magnet. This was followed by a loss of magnetic moment. In the case of drill rod steel after an hour the moment had fallen by about 4 per cent., the liquid being at 20° C. "From two to three hours' exposure to the electrolytic hydrogen decreased the magnetic moment of the magnet to a fixed value. Hammering the magnets had little or no effect in changing further their magnetic moment. Careful weighing before and after treatment showed that the magnets did not lose weight during exposure. . . . The rapidity with which the magnetic moment settles to a final value depends on the temperature of the electrolyte in which the magnets are brought under the action of the electrolytically evolved hydrogen. Moreover, the transition to the final state, due to the action of the hydrogen, is surprisingly different for the different specimens."

Special magnet steel, a tungsten alloy steel, after having been exposed for some time to the hydrogen, showed a sudden fall in the value of its moment. This was especially marked when the quenching occurred at 700°. One specimen lost in three minutes as much as 11 per cent. of its moment. The continuance of the treatment for eighteen minutes made scarcely any further difference.

When the magnets were broken the fracture showed that the hydrogen had penetrated within the steel. It is known that the magnetic permeability and also the specific resistance are modified by the process. G. F. S.

Research on Liquid Carbon Dioxide.—The Liquid Carbonic Division of the Compressed Gas Manufacturers' Association announces the establishment of an Industrial Fellowship in the Mellon Institute of Industrial Research of the University of Pittsburgh, for the purpose of classifying, studying and developing the uses for liquid carbon dioxide. The founding of this Fellowship is in accord with the desire of the members of the Association to coöperate with users and prospective users of liquid carbon dioxide, with the object of developing efficient means of applying the gas and of obtaining fundamental data bearing on its use in various industries.

In addition to conducting research work, the Fellowship will be made a clearing-house of information regarding various uses of liquid carbon dioxide, and data will be kept on file for the accommodation of prospective users of this product.

The present incumbent of the Industrial Fellowship is Charles L. Jones, who will be glad to correspond with anyone interested in the use of liquid carbon dioxide in industry.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, November 15, 1922.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 15, 1922.

MR. W. C. L. EGLIN, Vice-president, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of:

Robert Atkinson, Esq., Teacher, Haverford College, Haverford, Pennsylvania.

Gustav Egloff, Esq., Ph.D., Chemist, 208 South La Salle Street, Chicago, Illinois.

Walter M. Mitchell, Esq., Ph.D., Metallurgical Engineer, 112 North 34th Street, Philadelphia, Pennsylvania.

Harry K. Rutherford, Esq., Major, Ordnance Department, U. S. A., Frankford Arsenal, Philadelphia, Pennsylvania;

lectures before the Sections as follows:

"High-speed Photography of Vibrations" by
Augustus Trowbridge, Ph.D.,
Professor of Physics,
Princeton University,
Princeton, New Jersey,

"The Spectrum of Neutral Helium and the Behavior of Its Two Electrons" by
Ludwik Silberstein, Ph.D.,
Research Laboratory,
Eastman Kodak Company,
Rochester, New York,

"Structural Colors in Feathers" by
Wilder D. Bancroft, Ph.D.,
World War Memorial Professor of Physical Chemistry,
Cornell University,
Ithaca, New York,

and a lecture before the Stated Meeting October 18, 1922, by
Arthur L. Day, Ph.D., Director,
Geophysical Laboratory,
Carnegie Institution,
Washington, D. C.
on "The Study of Earth Movements in California;"

also additions to the library by gift, 23 volumes and 70 pamphlets, by purchase, 17 volumes and by binding, 128 volumes.

The Chairman then announced that final action would be taken on the following resolution to amend the By-Laws as recommended by the Board of Managers to the Institute at its Stated Meeting of October 18th last:

"RESOLVED, That the words 'in the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute,' in Section 1 of Article 1 be omitted and stricken therefrom, and that the last paragraph of Section 6 of Article 1, as follows: 'The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to its continuance and preservation,' be omitted and stricken therefrom, and that Section 1 of Article 1 and Section 6 of Article 1 be amended so as to read as now expressed with the omission of the said words."

On motion, duly seconded, the resolution was unanimously adopted.

Doctor Hoadley offered the following resolution which was seconded by Doctor Cope and passed unanimously:

"RESOLVED, That a committee of three be appointed to nominate officers and managers for the year 1923."

The Chairman then announced that the next business of the meeting would be the presentation of awards made by the Institute on recommendation of its Committee on Science and the Arts and recognized Dr. Thomas D. Cope.

Doctor Cope said, "Mr. Chairman, Members of the Institute, Ladies and Gentlemen: It is the custom of the Committee on Science and the Arts each year to review all the articles that have appeared in the JOURNAL OF THE INSTITUTE during the year, with a view to selecting for recognition those articles which appeal to the Committee as possessing especial merit.

"The highest award which the Committee is empowered to make for an article of superior excellence in the JOURNAL is the Howard N. Potts Gold Medal.

"For the year 1921, the Committee has selected the paper on 'Helium, Its History, Properties and Commercial Development,' by Dr. Richard B. Moore, Chief Chemist, United States Bureau of Mines. This paper appeared in the JOURNAL OF THE INSTITUTE for February, 1921.

"In this paper the romantic story of helium is completely and authentically told. In selecting this paper for the highest recognition, the Committee has not been unmindful of the fact that the author has witnessed the development of the story which he tells and has taken a foremost part in the making of that story.

"I have the honour, Mr. President, to present to you, Dr. Richard B. Moore, Chief Chemist of the United States Bureau of Mines, to receive from you the Howard N. Potts Medal for his paper on 'Helium, Its History, Properties and Commercial Development.'"

The Chairman then presented the Medal and Accompanying Certificate to Doctor Moore, who in acknowledging this recognition, said,

"Mr. President, Members of the Institute, Ladies and Gentlemen: I desire to thank you, the Chairman, and the Members of The Franklin Institute, most heartily for the honour conferred upon me. I naturally feel somewhat overwhelmed that this honour should have come from The Franklin Institute, and

I appreciate it all the more strongly because of my personal interest in the Institute, which has extended over a number of years.

"For your information I may say that at the present time about 15,000 cubic feet of helium is being extracted each day, and stored in tanks, and within a couple of months, I hope that this figure will be raised to between 30,000 and 40,000 cubic feet per day. As there were only about 10 cubic feet of helium in the world before the war, this represents some real progress even though we have a considerable way still to go."

The Chairman then recognized Dr. George A. Hoadley who introduced Dr. C. W. Colby, President, The Noiseless Typewriter Company, New York City.

Doctor Hoadley said, "Mr. President: It would be most interesting to know how man first began to formulate a spoken language by means of which he could communicate his ideas to his neighbor.

"Even more interesting would be accurate information as to how this primitive man first began to communicate these ideas to his neighbor when he was no longer present to hear the spoken word. That this was done we know, for crude carvings and clay tablets and stone records have come down to us.

"From these beginnings has developed the art of manually written language by the use of the pen and pencil. With the advancement of civilization and the increase of business correspondence came the demand for a more rapid method of communication than either the pen or the printing press could supply. This demand was met by the invention of the typewriter, many kinds of which are in use.

"One objectionable feature, common to these machines is the insistant and distracting noise of the hammer blow of the type against the platen in the process of typing, a blow for every letter.

"This feature called for removal and a typewriter has been devised, developed and placed within our reach that makes it possible to operate one or more of these Noiseless Typewriters in a room and still be enabled to carry on the other business of an office without interference. This is done by substituting for the hammer blow stroke a pressure stroke.

"'In consideration of the ingenuity shown by the inventors, the excellence of design and construction as exhibited in the machine, resulting in a thoroughly successful commercial noiseless typewriter, The Franklin Institute awards its Edward Longstreth Medal to The Noiseless Typewriter Company of New York.'

"Mr. President, I take pleasure in presenting Dr. Charles W. Colby, President of The Noiseless Typewriter Company, of New York."

The Chairman then presented the Medal, Certificate and Report to Doctor Colby who in acknowledging this recognition said:

"Mr. President, Members of the Institute, Ladies and Gentlemen: It was the saying of the Romans that there was no greater satisfaction in life than to be praised by one who is himself highly honoured; and it is because The Franklin Institute has been for so many years held in such high honour that The Noiseless Typewriter Company is profoundedly indebted to it for this high award.

"We are living in an age when the principle of authority is not perhaps so strong as at some periods in the past—perhaps not strong enough. But

fortunately The Franklin Institute is a source of authority and the credentials received from it confer international honour.

"This is not the place for a harangue about The Noiseless Typewriter, regarding which Doctor Hoadley has spoken so appreciatively. However, one may point out that the writing machine is an indispensable part of modern civilized life. It used to be said that the pen is mightier than the sword and, changing the terms somewhat, it may now be said that the typewriter is mightier than the machine-gun, but that is no reason why it should make as much noise as a machine-gun.

"The Noiseless Typewriter is not a vegetable product that grows in the woods, and it took twenty years of hard work to develop it. I am very happy to say that some of the engineers who have contributed most to its development —including Mr. Kidder, Mr. Ruffin and Mr. Going—have lived to see the result of their labours and are here this evening.

"As regards The Noiseless Typewriter Company, I may say that those who constitute its membership have not been actuated merely by a desire for commercial gain, but have felt that they were engaging in a useful, constructive work. No recognition received by our Company is as much appreciated as this honour bestowed by The Franklin Institute."

The paper of the evening on "Animal Luminescence" was then presented by E. Newton Harvey, Ph.D., Professor of Physiology, Princeton University, Princeton, New Jersey. A review of the general facts of animal luminescence was first given. The physical nature of animal light, its relation to inorganic luminescences, and the chemical processes underlying its production were also considered. Special attention was given to the factors determining the intensity of luminescence and the possibility of obtaining a continuous luminescence was discussed. The subject was illustrated by lantern slides and demonstrations.

After a brief discussion the unanimous thanks of the meeting were extended to the speaker.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, November 1, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, November 1, 1922.

DR. H. J. M. CREIGHTON *in the Chair.*

The following reports were presented for first reading:

No. 2793: Doctor Pfund's Physical Apparatus.

No. 2795: Johnson Hydraulic Valve.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A joint meeting of the Section and the Philadelphia Section of the Illuminating Engineering Society was held in the Hall of the Institute on Thursday evening, October 5, 1922, at eight o'clock, with Dr. Howard Lyon in the Chair. The minutes of the previous meeting were approved as published.

Herbert E. Ives, Ph.D., of the Research Laboratories of the American Telephone and Telegraph Company and Western Electric Company, Incorporated, New York City, New York, presented a communication on "The Primary Standard of Light." A description was given of the use of the brightness of the black body at the melting point of platinum as a primary standard. The lecture was illustrated by means of apparatus and lantern slides.

The communication was discussed at length; a vote of thanks was extended to Doctor Ives; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, October 26, 1922, at eight o'clock, with Dr. George A. Hoadley in the Chair. The minutes of the previous meeting were read and approved.

Augustus Trowbridge, Ph.D., D.S.M., D.S.O., Chev.L.H., Professor of Physics in Princeton University, delivered a lecture on "High-speed Photography of Vibrations." A summary was given of the essential features of both the recording and the indicating members of apparatus designed to record accurately minute and rapid vibrations of various types, such as sound, electrical and mechanical. The apparatus was exhibited, and was used to produce records of both simple and complicated vibrations made during the course of the lecture.

The application of the apparatus to the study of the pressure and volume changes in the cylinder of the modern high-speed internal combustion engine was shown by means of lantern slides.

The paper was discussed; a vote of thanks was extended to Doctor Trowbridge; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 2, 1922, at 8 o'clock, with Dr. Thomas D. Cope in the Chair. The minutes of the previous meeting were approved as read.

Ludwik Silberstein, Ph.D., of the Research Laboratory of the Eastman Kodak Company, Rochester, New York, delivered a lecture on the "Spectrum of Neutral Helium and the Behavior of its Two Electrons" in which he demonstrated that the two electrons in a helium atom do not disturb each other to any appreciable extent, either electron being mainly controlled by the nucleus only.

The paper was discussed; a vote of thanks was extended to Doctor Silberstein; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, November 8, 1922.)

RESIDENT MEMBERS.

DR. WALTER M. MITCHELL, 112 North 34th Street, Philadelphia, Pennsylvania.
MAJOR HARRY K. RUTHERFORD, Frankford Arsenal, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERS.

DR. GUSTAV EGLOFF, 1284-208 South La Salle Street, Chicago, Illinois.

ASSOCIATE.

MR. ROBERT ATKINSON, Haverford College, Haverford, Pennsylvania.

CHANGES OF ADDRESS.

MR. R. H. DAY, 505 W. Clapier Street, Philadelphia, Pennsylvania.
MR. W. L. GARRELS, Webster Groves, Route 5, Mason and Manchester Roads, St. Louis County, Missouri.
MR. FRANK GITTELSON, 3500 Holmes Avenue, Baltimore, Maryland.
MR. J. H. GRANBERY, American Car Company, Boston and Hudson Streets, Baltimore, Maryland.
MR. WALTER F. HAGAR, JR., in care of The Hagar Company, Ambler, Pennsylvania.
MR. T. C. MARTIN, Twinbrook Farm, Ringville, Massachusetts.
MR. C. P. SCHLICKE, 191 Berkeley Place, Brooklyn, New York.
MR. C. F. SULZNER, 131 N. E. Second Street, Miami, Florida.
MR. RALPH C. STEWART, Sydenham Building, 1512 Walnut Street, Philadelphia, Pennsylvania.
DR. C. C. THOMAS, 1111 Hollingsworth Building, Los Angeles, California.
MR. ROBERT L. WOOD, 218 South Sixteenth Street, Philadelphia, Pennsylvania.

NECROLOGY.

Mr. Morris Ebert, 1706 Green Street, Philadelphia, Pennsylvania.
Mr. A. L. Johnson, Mutual Life Building, Buffalo, New York.
Dr. John F. Kelly, 284 W. Housatonic Street, Pittsfield, Massachusetts.

LIBRARY NOTES.

PURCHASES.

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BOOK NOTICES.

THE ANALYSIS OF RUBBER, by John B. Tuttle. 158 pages and index, 8vo. New York, The Chemical Catalog Company. Price $2.50 net.

This is another volume of the American Chemical Society's Monograph Series, and follows as to size, type and general make-up, the previous volumes reviewed in this JOURNAL. The subject of the present work is one of great industrial and even social importance. The word "rubber," as applied to the materials now so familiar in the automobile tire, and long familiar in many other articles, is derived from its use in erasing lead pencil marks. The use in this sense dates from 1788, the pieces used for such purposes being termed "rubber" or "lead-killer." The latter uncouth phrase has fortunately been entirely forgotten. In the earlier uses, wild rubber, that is, the product of the plants growing without special care, was used, but to-day plantation rubber forms the bulk of the supply. In strict expression rubber is a polyterpene, an indefinite multiple of the ratio C_5H_8, but homologous forms exist. For each unit group of this formula there is one double carbon linking, and, therefore, the substance is capable of taking up certain negative elements. Upon this fact depends essentially the process of vulcanization. Many plants contain the rubber hydrocarbon or at least substances closely analogous. Even in temperate regions, milkweeds and spurges are frequently found containing such substances, but, of course, the low yield and the high cost of land and labor in such places precludes any exploitation, and even discourages scientific study. The hydrocarbons are generally found in a special system of vessels, the contents being classed by botanists as "latex." Of the tropical plants that yield a latex in such amount and of such quality as to constitute a commercial source, the *Hevea brasiliensis* Muell. Arg. is the most important. It belongs to the *Euphorbiaceæ*, a large group of plants, distributed over many parts of the world, many of which contain more or less latex. The specific name is spelled *Braziliensis* in the book, but the form *brasiliensis* is that used by botanical authorities and should be followed. English-speaking

persons are apt to forget that the systematic names of plants and animals are not English words, but Latin, and should follow in orthography and orthoepy, as far as possible, the Latin forms. Hevea rubber is the best of the wild form and is now raised in the plantations. The growth of the plantation industry since 1903, when 25 tons were produced, to 1919 when 360,000 tons was the total, is shown in a table. Hevea rubber became known as Para rubber from the Brazilian port from which it was largely exported. The author of the work tells us that now-a-days cultivated rubber can be produced so cheaply that the poorer grades of wild rubber are but little sold, and even the better grades thereof have suffered from the competition of the plantation product. He thinks that in many cases the specifications, often insisted on, for Para rubber are not necessarily complied with.

While the main constituent of rubber is the hydrocarbon, small amounts of other substances are always present. Hevea rubber contains from 2 to 4 per cent. of resins, most of which are saponifiable and soluble in the common organic solvents. The best rubbers are clean and dry and have no appreciable ash. Rubber, of course, is liable to much adulteration. The vast array of articles manufactured from it are likely to contain many substances, some added properly in the course of manufacture, others as mere cheapeners. The analysis of commercial rubber and rubber products is, therefore, a complicated problem, but one to which a great amount of attention has been given and which to-day is in an advanced state of development. The extensive literature in journals and books has been gone over by the author and presented in this volume in compact form.

The present work is primarily addressed to the chemists in the laboratories of incidental consumers of rubber, but it is a comprehensive and careful summary of the trustworthy processes, and will be welcome to the more thoroughly trained chemists of the establishments concerned directly with the product. The field is very extensive and the enormous amount of data at hand has been sifted with care, giving to the worker a concise and large amount of information both as to the procedures and the nature and properties of the commercial forms of raw and manufactured articles.

One of the most important, perhaps really the most important step in the utilization of rubber, is the application of vulcanization. By this method many degrees of hardness can be obtained, and rubber thus became applicable to very many uses. Of course, the great boom in its use is due to the automobile, and it is interesting to note how the production of the raw material has kept pace with the demand. It is fortunate for the automobile industry that the plantation system has been capable of such great expansion.

Only limited space is given to the question of rubber substitutes. This matter is probably not of very great importance just now when the price of good rubber is low. Should the demand get materially in excess of the supply, renewed attention will be given to the research for substitutes or the synthetic production of the hydrocarbon. A bibliography is appended. It is extensive and arranged alphabetically by authors. It is a question whether such an arrangement is a good one. For any searching for particular data in the field, it seems that a classified list would be best.

HENRY LEFFMANN.

A CONCISE PHYSICS FOR ENGINEERING STUDENTS. By John E. Hoyt, Ph.D., assisted by Charles A. Bareuther, B.S., C.E., and N. M. Chamberlain, B.S., A.M. 385 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1922. Price, $2.50.

Anyone who undertakes to write a concise book on the subject of physics needs to be an adept in knowing what to omit.

When such a book is written for the purpose of being used as a text by students of engineering, there is an added difficulty on account of the fact that nearly all engineering is applied physics.

The subjects retained must be those of fundamental importance to the engineer and should be treated not only concisely, but with sufficient clearness to be readily understood.

The authors seem to have met these requirements, no small share of the credit being due to the extended lists of practical problems that are given for solution.

GEO. A. HOADLEY.

COLOUR INDEX, Part I. Edited by F. M. Rowe, D.Sc., F.I.C. 24 pages, quarto. Bradford, England, Society of Dyers and Colourists, 1922.

From the statement printed at the upper right-hand corner of several of the earlier pages, "Not to be bound with the completed volume," it is to be inferred that the present publication is rather suggestive than final. It is the initiative of a comprehensive catalogue of dyes especially arranged for users of these materials. Each dye is given a number, which does not agree with that given in the long-known "Tabellen" of Schultz, but in each case the Schultz number is given in parenthesis. It is not stated in the preface what motive has led to changing the numbers, but presumably it is the introduction of new dyes. Fast green O is number one in each list, and fast printing green, number 2, but the coincidence ceases at the latter point, and ultimately the difference becomes quite wide as 18 on the present list is 149 on Schultz. The scheme followed in the work is that now usual in such lists. Each dye is given a series of blocks with synonyms, scientific name and structural formula, when the latter is known, method of preparation, name of discoverer, important bibliography, general description, properties, and methods of use. The collection and arrangement of these data represents a great deal of labor, notwithstanding the tables and summaries already available. Extended tables are given of abbreviations for firm names, periodical literature cited and patent references. It is noted that the familiar BASF is here reduced to B. The type and printing are very satisfactory. The space limitations have necessitated a very small type in many entries, but these are easily readable. It is also to be noted that A. P. does not stand for American patent, but Austrian. What are commonly in this country called American patents are in this list designated U. S. P. Our government has officially adopted the term American as the designation in international affairs, such as our ambassadors, ministers and consuls, but some foreign nations, including Great Britain, have not accepted this plan, and in the diplomatic correspondence that took place during the war, some amusing see-sawing of official titles occurred.

The pamphlet in hand is, as noted, but a preliminary issue; the entire work will be extensive and useful. It will mark another step in enfranchisement from German control of the nations that constituted the group known as "The Allied and Associated Powers." Whether rivalries between these constituent nations will arise remains to be seen, but the economic struggle that was at the basis of the great war—and is at the basis of all wars—is influential in all countries. Circumstances often alter allies. However, the appearance of this pamphlet is a matter of congratulation by English-speaking chemists, and it is evident that it is the first pages of a very valuable and useful book.

HENRY LEFFMANN.

THE SUBJECT INDEX OF PERIODICALS, 1917–19. Issued by the Library Association. Part K, Science and Technology. London, The Library Association, 1922. 555 pages, 4to. Price, £1 15 schillings net.

Pope was in humorous mood when he noted

"How index learning turns no student pale,
But holds the eel of science by the tail,"

but the remark is a truism, for in the conditions of modern scientific development reference volumes, such as that under review, are absolutely necessary. The value of such works depends so largely upon the promptness of their appearance, that one is at first inclined to look with some disfavor upon an index extending only to three years prior to its appearance, but allowance must be made for several interfering conditions not the least of which has been the war. It is wise that the *terminus ad quem* should be the end of a calendar year, which necessitates waiting until the given year is completed. The collection and verification of the data will require a great deal of time, and the transcribing and printing will also delay publication. Accuracy in references and thoroughness in scanning the literature are, of course, of primary importance, but in recent years these procedures have been carefully followed and the indexes now before the public are mostly quite satisfactory.

The volume before us is one of a series which is presumably intended to cover a very wide range of literature. K, the section in hand, is devoted to Science and Technology. It contains an enormous number of entries clearly and conveniently arranged. A slip attached to the title page states that there is a total of 15,000 entries obtained from the examination of more than 400 periodicals. The references are classified by subjects arranged alphabetically. A high degree of subdivision with the use of a very distinct type for all headings greatly aids the searcher, and adds to the value of the book. The work is highly creditable to all who have had a share in its production.

HENRY LEFFMANN.

LE BEAU, LE MAUVAIS TEMPS ET LA RELATIVITÉ, par P. Drosne. 68 pages, 4½″ x 7″, paper. Paris, Gaston Doin, 1922. Price, 3 Francs 50 net.

Relativity is the fashion, in fact, scientific minds have recognized fully that a new doctrine has appeared, under conditions in some respects extremely modest and yet in others, courageous. According to M. Drosne the indisputable and undisputed point is that the classic science (meteorology) has arrived at

a decisive turning point in its history. He has endeavored to show the enormous progress which will be obtained when it is decided to state its problems in terms of relativity. In his opinion it is not "till then that we will know what we are saying and what we are calculating. No relativity, no salvation."

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 150, Pressure Distribution over Thick Aerofoils. Model Tests by F. H. Norton and D. L. Bacon. Langley Memorial Aeronautical Laboratory. 22 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This investigation was undertaken in order to study the distribution of loading over thick wings of various types. The loading on the wing was determined by taking the pressure at a number of holes on both the upper and lower surfaces of a model wing in the wind-tunnel. The results from these tests show, first, that the distribution of pressure over a thick wing of uniform section is very little different from that over a thin wing; second, that wings tapering either in chord or thickness have the lateral centre of pressure, as would be expected, slightly nearer the centre of the wings; and, third, that wings tapering in plan form and with a section everywhere proportional to the centre section may be considered to have a loading at any point which is proportional to the chord when compared to a wing with a similar constant section. These tests confirm the belief that wings tapering both in thickness and plan form are of considerable structural value because the lateral centre of pressure is thereby moved toward the centre of the span.

Report No. 154, A Study of Taking-off and Landing an Airplane, by T. Carroll. Langley Memorial Aeronautical Laboratory. 7 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report covers the results of an investigation carried on at the Langley Memorial Aeronautical Laboratory for the purpose of discussing the various methods of effecting the take-off and the landing of an airplane, and to make a direct analysis of the control movements, the accelerations, and air speeds during these manœuvres. The recording instruments developed at the laboratory were used in this test and the records obtained by them were made the basis of a comparative study of the two extreme methods of taking-off (the tail-high and the tail-low methods) and of various types of landings. It is believed that this is the first time that an accurate record has been obtained of the movements of the controls during these important manœuvres, and the records are of further interest from the fact that they were taken synchronously with records of the air speed and acceleration.

The records themselves should be of considerable value to a student pilot in enabling him to visualize the movements of the controls and the consequent effect upon the air speed and acceleration. This opens a very important field for research in the study of the technic of piloting, either of student pilots or for the "refresher" courses or other checking up of pilots in general. With these instruments it will be possible to obtain records of the manœuvring of any pilot in practically any type of airplane, and from the records so obtained any fault or roughness can be immediately noted. This can be done not only in the manœuvres of taking-off or landing, but in any sort of straight flight or "stunting."

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Mèthodes et Problémes de Théorie des Fonctions, par Émile Borel. 148 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 12 Francs.

Cours de Physique Mathèmatique de la Faculté des Sciences, par J. Boussinesq. Compléments au Tome III. 217 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 30 Francs.

Library Association: The Subject Index to Periodicals, 1917–1919. Part K, Science and Technology. 555 pages, quarto. London, The Library Association, 1922. Price £1 15s. net.

Society of Dyers and Colourists: Colour Index. Part I. Section A, Synthetic Organic Dyestuffs. 24 double pages, quarto. Bradford, England, Society, 1922.

A Concise Physics for Engineering Students, by John E. Hoyt, Ph.D., assisted by Charles A. Bareuther, B.S., C.E., and N. M. Chamberlain, B.S., A.M. 385 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1922. Price $2.50.

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Water Supply Installations for Farmsteads and Country Estates, by William Paul Gerhard, C.E., Dr.Eng. 24 pages, 8vo. New York, Author, 1922. Price forty cents.

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United States Public Health Service: Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide, by R. R. Sayers, F. V. Meriwether and W. P. Yant. Reprint No. 748 from the Public Health Reports. 16 pages, plate, 8vo. Washington, Government Printing Office, 1922. Price five cents.

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National Advisory Committee for Aeronautics: Technical Notes No. 115, The Effect of Longitudinal Moment of Inertia upon Dynamic Stability, by F. H. Norton and T. Carroll, Langley Memorial Aeronautical Laboratory. 3 pages, photograph, quarto. No. 116, F-5-L Boat Seaplane. Comparative Performance with Direct Drive and Geared Engines. Compiled by Lieut. W. S. Diehl, Bureau of Aeronautics, U. S. N. 12 pages, quarto. Washington, Committee, 1922.

CURRENT TOPICS.

The Curve of Energy Distribution in the Ultra-violet Part of the Solar Spectrum. C. FABRY and H. BUISSON. (*Comptes Rendus,* July 17, 1922.)—"The distribution of energy in a continuous spectrum can be determined by using some thermometric instrument as the apparatus for measuring the energy. This direct method necessitates the employment of delicate apparatus and cannot be applied except under conditions rarely realized in our laboratories. Moreover, the thermometric arrangement for receiving energy has only a feeble power of definition. This is in itself a grave drawback in the study of the solar spectrum, which is crossed by absorption lines that are very close together in places. These difficulties explain why the energy curve of the solar spectrum is so little known in the region of small wave-lengths where the experimenter is confronted by the presence of but a small amount of energy in a spectrum having numerous dark lines and by a strong absorption by the earth's atmosphere. Abbot's measurements, which are the most complete of all those made on the solar spectrum, are very uncertain in this part of the spectrum."

It is for such reasons that the French savants have selected for their work a method less direct, it is true, but more easy and certain in its application. They proceeded by making comparisons with an artificial source of radiation of which the energy distribution curve was known. The intensities of the light from the two sources were compared for several wave-lengths and from their ratio at a selected wave-length and the known energy of one source it was possible to calculate the energy of the other for that frequency. Many sources of error drop out of consideration in this method, but it is required to know thoroughly the energy distribution of the standard with which comparison is made. Fortunately the law of radiation of a black body is well known and certain solid bodies are sensibly identical in their radiation with a black body. Such a solid is the positive crater of the electric arc, and 3750° was taken as its temperature. On the slit of the spectrograph were projected in turn the image of the crater and that of the sun. The intensity of the latter could be reduced in a known proportion by the use of diaphragms or of absorbing screens. The opacity of the two images on the photographic plate was measured by a microphotometer and from the results was calculated the ratio of the intrinsic brightness of the two sources of light. At different hours of the same day the comparison was repeated in order that the coefficient of atmospheric absorption might be determined and that, further, the intensity of the sunlight outside of the atmosphere might be computed.

Determinations were made for five wave-lengths ranging from

3940 to 2922. The coefficients of atmospheric absorption had a corresponding range from .32 to 4.82. The significance of this last figure is the following. When sunlight is passing vertically down through the air, only one part in 70,000 of the energy at wave-length 2922 gets to the surface of the earth.

From each of the five comparisons the temperature of the sun is deduced in terms of the absolute scale. The highest value is 6016° and was got from the longest wave-length while the lowest 5832° came from the third of the five. The next-to-highest temperature was derived from the shortest wave-length.

Below the wave-length 2900 all observation is impossible by reason of the enormous atmospheric absorption. There seems to be no reason for hesitating to assume, even in the absence of actual measurements, that the sun emits wave-lengths shorter than 2900 about as a black body at the temperature of 6000° abs. emits them. "If this be so, the importance of the radiation that cannot be observed is far from negligible. The energy emitted by the sun in the form of radiation having wave-lengths inferior to 2900 is one-twenty-fourth of its total radiation and about one-quarter of its total radiation is ultra-violet, that is, of wave-length less than 4000 Angstrom units." G.F.S.

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